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Infrared Spectroscopic Studies on Structure and Dynamics of Organic Functional Thin Films

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Infrared Spectroscopic Studies on Structure and Dynamics of Organic Functional Thin Films

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Deo favente et naturalis altiudine et amans Fusako concepi.

INTRODUCTION

The purpose of this thesis is to provide new insight into structure and dynamics of two kinds of organic functional thin films, *i.e.*, Langmuir-Blodgett (LB) films and Liquid Crystals (LCs). The functions of the organic thin films strongly depend upon the structure and orientation of the molecule consisting of the films and interaction between the molecule and substrate surface. In Figure 1 is shown an illustration of organic functional thin films studied in this thesis. Structural and orientational changes influence their physical and chemical properties, so that one can utilize them into new types of materials, such as chemical sensors and electronic devices. For instance, a liquid crystal display (LCD), which recently made marked progress, takes advantages of the reorientation of the LC molecule as illustrated in Figure 2. Macroscopic studies have been carried out for investigating on dynamics of the reorientation [1,2], while the microscopic investigations on dynamics are required to elucidate the mechanism of the structural and orientational changes. Therefore, the structural characterization of the thin films is fundamentally important for the studies of the functional thin films. I have applied Fourier transform infrared spectroscopy to investigate the molecular structural studies of those organic films. This technique is a beneficial mean to prove the molecular and electronic structure of the thin films *in situ*. Furthermore, time-resolved infrared spectroscopy, which has recently been developed, is progressive tool for dynamic studies of the structural and orientational changes of the thin films. Accordingly, the characteristic study by infrared spectroscopy is quit

useful for the static and dynamic descriptions of structure-function relationships of the organic thin films.

Thin films perform peculiar property which is quite different from that in bulk state. Especially, thin films composed of organic compounds are expected to behave in novel functions for academic and industrial objects. These behavior of organic thin films strongly connected with the property of substrate surface adhering to the film as well as the property of the compound in the state of thin film. The nature of surface fills an essential role as an intermediary between the substance and substrate. Hence, the novel property of the thin films is under the influence of the circumstances, *i.e.*, structure, configuration, and orientation. A new phenomenon will appear along with the control of these conditions.

LB films, presented by Langmuir and Blodgett in 1935 [3,4], are monolayer assembly films that hold considerable promise as artificial superamolecular organizers with planned structure and properties [5-8]. It may become possible to control the construction of functional organic materials at the molecular level. Various molecular devices have been proposed that are based on LB films, such as films with nonlinear optical properties, photovoltaic cells, piezoelectric and pyroelectric devices, resistance and conducting materials, and chemical and biological sensors [6-8]. To understand the interesting physical properties of LB films and to design new films with more desirable properties, structure-function relationships of the films must be investigated. Molecular conformation, orientation, aggregation, and electronic structure in molecules forming an LB film are deeply concerned with the properties. The interaction

between the first monolayer and substrate surface also may affect them. In addition, the structure depends upon the conditions for LB film preparation such as substrate substance, surface pressure, and built-up method. Structural changes in the LB films are interesting from both physical and chemical points, and comparison of the structure among solid states, spread monolayers on the water surface, and LB films is very important.

With the growth of LB film studies, the development of powerful structural probes which provide new insight into the structure-function relationship has become more and more important. The structural characterization of LB films have been performed extensively by X-ray [9,10] and electron [11] diffractions and electron microscopic techniques [12]. Recently, an atomic force microscopy (AFM) [13], a replica pattern method [14], and a new plasma-induced polymerized film replica technique coupled with transmission electron microscopy [15] have been introduced into morphological investigation of LB films. UV-visible absorption [16,17], fluorescence [17], and Raman [18,19] (including surface enhanced Raman scattering (SERS) [20,21]) spectroscopies have also been executed to the studies on molecular structure. FT-IR spectroscopy, presented in this thesis, is unique and powerful tool to investigate the structure of LB films at points of its superior sensitivity and much information provided. The advantages of the FT-IR technique are described later.

In 1968, Heilmeier reported that LCs begin to play its interesting behavior such as a reorientation by the electric field when they are confined into thin layer [22]. There has been wide-spread use of LCs in

display devices as they can be readily oriented by applying an external electric field and exhibit various electro-optic effects. Thus, the development of advanced display systems and the search for required new materials have constituted a major part of liquid crystal research for the past decades. Despite this excitement about new applications, our understanding of the elementary molecular mechanism of the electric-induced transition in liquid crystals is still limited. In particular, the local conformation and transition dynamics of rigid segments constituting a flexible liquid crystalline molecule is not yet clearly elucidated. Acquisition of such knowledge is of essential importance toward further progress in both the science and technology of LCs, and this necessitates a new experimental technique that enables us to interrogate about the details of field-induced phenomena of LCs at the molecular segmental level.

The interaction between the LC molecule and surface of substrate performs grave influence as well as that between the LC molecule and the electric field. It has long been recognized that the nature of the substrate surface plays an important role on the alignment of LCs. Amphiphilic reagents have been frequently introduced to substrate surfaces to promote LC alignment [23]. Although orienting mechanism of LCs have not been fully understood, the geometrical factors of surfaces and surface energy have been considered to account for the orientational behaviors. To discuss the role of amphiphiles on LC orientation on a molecular level, amphiphile molecules should be introduced onto surfaces in molecularly controlled manners. The LB technique is one of the tool for this purpose [24,25]. Ichimura *et al.* have recently been presenting a new method of reversible LC alignment regulations that are triggered by photochromic

reactions taking place on substrate surfaces [26-28] (Figure 1B). For azobenzene layers, the conformational change of *cis-trans* photoisomerization induces alignment changes of planar-homeotropic alignments. They have termed these photofunctional surface 'Command Surface' because this phenomenon involves marked amplification in the number of molecules (*ca.* 10^4-fold amplification) from commanding photochromic surface units to obeyed LC molecules [26]. Understanding the 'Command Surface' phenomenon on the molecular level requires another approach of the LB technique that is capable of giving molecularly tailored photochromic layers.

In 1975, a first ferroelectric liquid crystal (FLC), *p*-decyloxy benzylidene-*p*-amino-2-methylbutylcymmanato (DOBAMBC), was synthesized by Meyer *et al.* [29]. After then, in 1980, Clark and Legerwall developed a new type of electric device, *i.e.*, surface stabilized FLC display, consisted with the FLC molecule into a thin LC cell [30]. In the last few years the properties of FLC materials with chiral smectic C phase attracted increasing interest because of their fast (μs order) and efficient electric-optical response and a memory effect. They show potential as the electrically active media in a wide variety of application, such as displays, light-valves, spatial light modulators, and optical processing [29-31]. However, one of the basic problem of FLCs is the dynamics of FLC molecules when respond to an applied electric field which is not well-understood. The orientation behavior of FLC is so complicated compared with that of nematic LC, that various approach must be required to realize of the mechanism.

FT-IR spectroscopy, which affords structural information such as

molecular orientation, subcell packing, and electronic structure in a nondestructive manner, has recently been employed for the structural characterization of the organic thin films [32]. The FT-IR technique has a worth of special mention in its sensitivity, which allows one to obtain informative signals even from single-monolayer films. The advantages of FT-IR spectroscopy for investigating molecular orientation and structure of organic thin films include the followings: (1) Infrared spectra of the films can be measured nondestructively under normal temperature and pressure conditions. (2) Infrared spectroscopy can be applied to samples in various physical forms such as LB films, solids, crystalline phases, liquid crystalline phases, and solutions, making it possible to compare the structure of a sample in the form of a thin film with that in some other states. (3) Various infrared techniques such as reflection-absorption (RA) and attenuated total reflectance (ATR) can be used. Polarized infrared method provides an information of anisotropy of the films. (4) Even single-monolayer films of nano-meter thickness show spectra of sufficient quality to investigate the structure. (5) Vibrational spectroscopy can provide information of conformation, electronic structure, chemical bondings, and so on; infrared spectroscopy, particularly, suits with the investigation in molecular segments level individually, such as carboxylic group, azo group, and hydrocarbon chain.

As for LC, time-resolved infrared technique has been recently used to study the correlation between molecular dynamics and the structure of LCs [33,34]. Some dynamical studies have been reported by use of a dispersive time-resolved infrared technique [35]; while other reports have

been presented by means of time-resolved FT-IR (TRFTIR) methods [36-39]. Existing TRFTIR spectroscopy can be classified into three types. One is based on the conventional continuous-scan (rapid-scan) interferometer [40], another uses the step-scan interferometer [37,41], and yet another is an asynchronous time-resolved method. [36] In the case of rapid-scan method, an A/D converter serves for time resolving as well as for acquiring interferogram data. This arrangement not only imposes some restrictions on the mechanical aspect of the interferometer but also requires software completely different from that used for static measurements. In the case of step-scan, the interferometer of this method has a practical disadvantage in its complicated manipulation of the interferometer. On the other hands, the asynchronous time-resolved FT-IR spectrophotometer does not require synchronization between the signal for time resolving and that for the sampling of the A/D converter. In this method, the signal-processing assembly for time-resolved measurements can be attached to any FT-IR spectrophotometer, and this simple addition enables time-resolved measurements without any further modifications in either hardware nor software of the existing instrument. Moreover, there is no shortest limit in time for transients phenomena to be measured by this method, in principle, if an appropriate infrared detector could be obtained. This method allows sufficiently accurate measurements of both broad and sharp bands, keeping all the essential features of continuous- and step-scan FT-IR spectrometers such as the multiplex and throughput advantages. In contrast with FT-IR techniques, an ac-coupled dispersive time-resolved infrared technique has been developed by Hamaguchi *et al.* [35]. This technique is essentially benefit to measurements on response

curves of individual absorption bands, so that the time-resolution as high as 50 ns has been achieved with the minimum detectable absorbance change $\Delta A \sim 10^{-7}$. A comparison between the asynchronous TRFTIR and dispersive time-resolved infrared spectroscopies for studying dynamics of FLC is one of the major purposes of the present thesis. Accordingly, the former technique has been applied to the measurements of transient spectra for orientation of FLC, while the latter has been performed to the investigation of absorbance changes of certain bands.

This thesis can be divided into three parts.

In PART I, structural and orientational characterizations of LB films consisting of azo dye are described. It is demonstrated for the first time that two kinds of amphiphilic molecules, which have the same chromophoric part but are different from each other in the number of the hydrocarbon chains bonded (in the case of Azo I and Azo II), give similar but significantly different aggregation, orientation, and structure when the LB films are formed; for example, Azo I does not form an H-aggregate in the LB films while Azo II forms it; the hydrocarbon chains of Azo II have highly ordered (*trans*-zigzag) structure but that of Azo I is slightly less ordered in the films; the conformation and structure of Azo I chromophore change little among the LB and cast films and solutions while those of Azo II alter significantly between the LB films and the latter two states. This sort of comparative structural study may offer new insight into molecular design of LB films. Investigation of temperature dependence of molecular structure in the LB films is also presented in connection with their thermal stability. This is the first time that the order-disorder transition of LB film having a large

chromophoric part has ever studied. It is shown that alkyl chain mobility begins to increase with elevating temperature before their conformational disorder occurs, and the order-disorder transition of the tail groups is linked with the conversion from the H-aggregate to the monomers in the chromophore.

In PART II of this thesis, molecular orientation and anisotropy in 'Command Surfaces' formed by LB films of azobenzene amphiphilic polymers are reported. The infrared technique is applied for the investigation of the mechanism of photoregulations and reorientation of LC molecules controlled by the LB films. A reversible homeotropic-planar photochemical alignment controls of nematic LC is uniquely observed. The structural characterization of the LB films is also denoted in this part. Comparison of band intensities between the infrared transmission and RA spectra of the LB films indicates that the hydrocarbon chain assumes rather randomly oriented, which is profitable for an induced fitting between the host layer and guest LC molecules. Polarized FT-IR spectra obtained show that the anisotropy of the LB film in the *cis* form reflects the polarization of the irradiation lines photoregulated. The polarized infrared spectra also suggest that the anisotropy induced by light illumination is superior to that imposed during dipping process.

Two types of time-resolved infrared spectroscopic studies of electric-field-induced reorientation of ferroelectric liquid crystals (FLCs) are presented in PART III. Dynamical studies of the reorientation of FLCs are performed by using of an asynchronous time-resolved FT-IR spectrophotometer, while an investigation of preliminary process of the

reorientation by dispersive sub-microsecond time-resolved infrared method is also presented in this part. I first demonstrated that the influence of temperature and voltage of electric-field for the reorientation to realize the mechanism of reorientation of FLCs. These studies suggest that whole parts of FLC molecule reorients simultaneously as a rigid rod. An alteration of orientation mechanism in spontaneous polarization inversion was predicted by the investigation of temperature dependence. Furthermore, a time delay for counter-reorientation with short pulse electric field induced is detected by the dispersive time-resolved infrared technique. The investigation of the preliminary process of reorientation of FLC has never been carried out on molecular segments level so far.

The spectroscopic studies of the dynamics as well as the structural characterization of organic thin films throughout the present thesis may provide new insight into functions of the thin films and promote the development of new functions.

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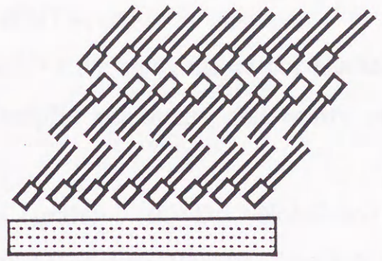
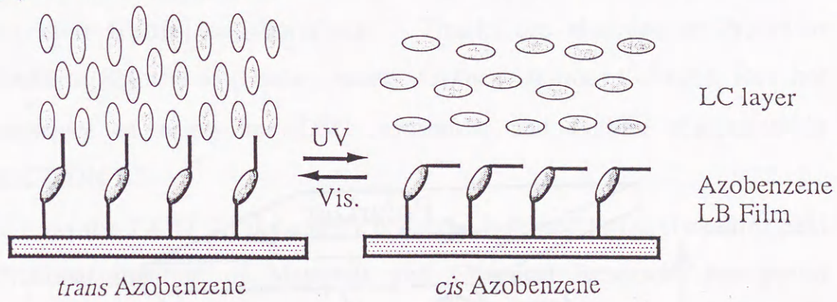
(A) LB film



(B) Command Surface



(C) LC cell

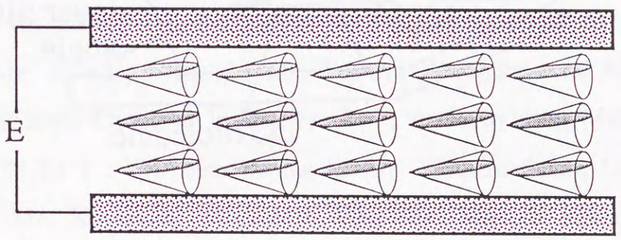


Figure 1. Schematic illustration of organic functional thin films; (A) Langmuir-Blodgett film, (B) Command surface, and (C) Liquid crystal cell.

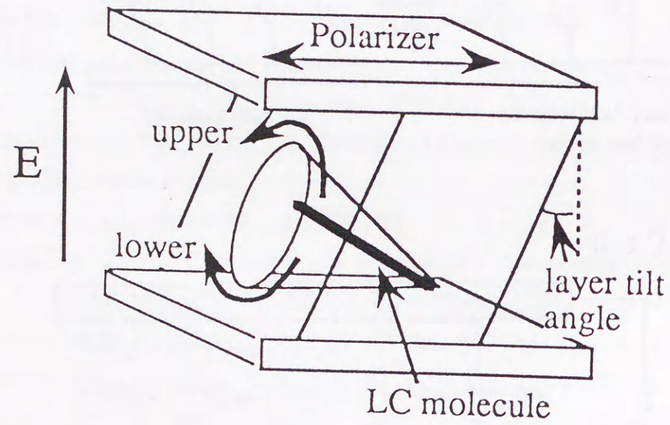


Figure 2. A model of reorientation of FLC molecule.

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PART I: Molecular Structure, Orientation, and Aggregation in Langmuir-Blodgett Films of Azo Dyes Studied by Infrared, Visible Absorption, and Resonance Raman Spectroscopy

SECTION I-1: Infrared Study of Langmuir-Blodgett Films of 2-(4'-Ethyloctadecylaminophenylazo)-N-methylbenzothiazolium perchlorate and 2-(4'-Dioctadecylaminophenylazo)-N-methylbenzothiazolium perchlorate

ABSTRACT

Infrared transmission and reflection-absorption (RA) spectra have been measured for Langmuir-Blodgett (LB) films of 2-(4'-methylocta decylaminophenylazo)-N-methylbenzothiazolium perchlorate (Azo I) and 2-(4'-dioctadecylaminophenylazo)-N-methylbenzothiazolium perchlorate (Azo II) to compare their molecular orientation and structure in the LB films. A comparison of the infrared transmission and reflection-absorption (RA) spectra indicates that the benzothiazolium rings of Azo I and Azo II are fairly perpendicular to the substrate surface but their benzene rings are tilted appreciably. As for the hydrocarbon chains, the infrared transmission, polarized transmission, and RA measurements suggest that the chains of both compounds are neither perpendicular nor parallel to the substrate surface, being tilted with respect to the surface normal and they are in a hexagonal or pseudohexagonal subcell packing with an uniaxial orientation. Vibrational frequencies of infrared bands due to CH_2 antisymmetric and symmetric stretching modes indicate that Azo II molecules in the LB films have highly ordered (*trans*-zigzag) hydrocarbon chains but Azo I molecules in the films have slightly less ordered chains. Probably, Azo II with two hydrocarbon chains is more easily ordered in the films than Azo I with one hydrocarbon chain.

INTRODUCTION

In recent years, interest in Langmuir-Blodgett (LB) films has been increasing greatly because of their possibilities as functional molecular devices such as electronic, nonlinear optical, and pyroelectric elements [1-3]. The increase in the interest has accelerated not only functional studies but also structural studies of LB films. A number of physical techniques have been introduce to the structural characterization of the molecular assemblies. We have been investigating the structure of LB films consisting of functionally important dye molecules by means of infrared and resonance Raman spectroscopy [4-8]. Infrared [9-21] and Raman [22-33] spectroscopy, which are both powerful nondestructive structural probes for various kinds of molecular assemblies in various conditions, provide information about the orientation, conformation, and electronic structure of molecules in the LB films and about interaction between a substrate and molecules. The information derived from the two spectroscopy is from time to time complementary to each other, and therefore a combined infrared and Raman study is, in general, very useful for the structural characterization of the LB films.

Infrared and resonance Raman studies on LB films of 2-(4'-ethyloctadecylaminophenylazo)-N-methylbenzothiazolium perchlorate (Azo I; Figure 1) and 2-(4'-dioctadecylaminophenylazo)-N-methylbenzo thiazolium perchlorate (Azo II; Figure 1) are discussed here and in the next section, respectively. Azo I and Azo II have the same chromophoric part but are different to each other in the number of the hydrocarbon chain bonded; Azo I has one hydrocarbon chain while Azo II has two hydrocarbon chains. It is of particular interest to investigate changes in

the molecular aggregation, orientation, and structure induced by the change in the number of the hydrocarbon chain. This sort of comparative structural study may offer new insight into molecular design of LB films.

EXPERIMENTAL

The compounds of Azo I and Azo II were synthesized by Kuramoto *et al.* [34]. A Kyowa Kaimen Kagaku Model HBM-AP Langmuir trough with a Wilhelmy balance was employed for the π-A isotherm measurements as well as LB film fabrications. The Azo I or Azo II monolayer was spread from a dilute chloroform solution (2×10^{-3} M) on doubly distilled water containing 1.4×10^{-4} M $CdCl_2$ and 1.7×10^{-5} M $NaHCO_3$ (pH 6.3, 20 °C). After evaporation of the solvent, the monolayer was compressed at a constant rate of 20 $cm^2 min^{-1}$ up to the surface pressure of 35 mN m^{-1}. The π-A isotherm showed that the monolayers were solid condensed films at this pressure. The LB films were prepared on CaF_2 plates (for transmission measurements) and Au-evaporated glass slides (for RA measurements). The latter slides were prepared as follows; after chromium of 150 nm in film having a thickness of 300 nm was evaporated onto it. The Au-evaporated glass plates thus prepared were rinsed well with hot isopropyl alcohol and then with acetone.

The transfer ratio was found to be nearly unity (0.95 ± 0.02) throughout the experiments. The LB film assemblies thus prepared have Y-type structure with the first layer in the "tail-on" (Azo I) or "head-on" configuration (Azo II).

Infrared spectra of the LB and cast films were recorded with 4 cm^{-1} resolution on a JEOL JIR-100 FT-IR spectrometer equipped with an MCT detector. Generally, several hundred scans were accumulated for

acceptable signal-to-noise ratio. For the RA measurements, a JEOL IR-RSC 110 reflection attachment was employed at the incidence angle of 80° , together with a JEOL IR-OPT02 polarizer. Polarized spectra were measured with the aid of the same polarizer. Infrared spectra of powdered samples were obtained using a micro infrared attachment (JEOL IR-MAU 110).

RESULTS AND DISCUSSION

Infrared Spectra of Azo I and Azo II in solid States

Figure 2 shows infrared transmission spectra of Azo I and Azo II in solid states. Intense bands at 2923 and 2851 cm^{-1} are assigned to CH_2 antisymmetric and symmetric stretching modes of the hydrocarbon chains and a medium one at 2953 cm^{-1} is due to their CH_3 asymmetric stretching mode. Comparison of the infrared spectra in Figure 2 with those of benzene- [35,36], azobenzene- [36-39], and cyanine [40] derivatives enables us to propose vibrational assignments for several bands in the 1700-800 cm^{-1} region. Bands at 1611 and 1520 cm^{-1} may be assigned to a $^{+}N=C$ stretching mode and ν_{19}-like mode of the benzene ring, respectively, as in the case of resonance Raman spectra of Azo II [8]. A medium feature at 1468 cm^{-1} may be due to a CH_2 scissoring mode of the hydrocarbon chains because the relative intensity of this band is much stronger in the spectrum of Azo II which has two hydrocarbon chains. It is well known that azobenzene derivatives give a band due to a =N-Ph stretching mode near 1150 cm^{-1} [36-39]. Therefore, a band at 1163 cm^{-1} of Azo I and one of two bands near 1165 cm^{-1} of Azo II probably arise from the =N-Ph stretching mode. There is little doubt that a band near 841 cm^{-1} is due to a CH out-of-plane deformation mode of the benzene ring [35,36]. An intense band near 1095 cm^{-1} is ascribed to ClO_4^- [40].

The infrared spectra of Azo I and Azo II in the solid states are, in general, very similar to each other except for the relative intensities of

the bands arising from the hydrocarbon chains. However, there is significant difference in the band contour in the 1175-1150 cm^{-1} region between the two spectra. Since the structure of Azo I and Azo II is different only in substituent of the nitrogen atom which is bonded to the phenyl ring, the difference in the 1175-1150 cm^{-1} region may come from the change of the substituent. Thus, one of the two bands near 1165 cm^{-1} of Azo II was tentatively assigned to the Ph-N stretching mode.

Infrared Spectra of Azo I LB Films

Figure 3(A) exhibits infrared transmission spectra of the 2-, 4-, and 10-monolayer Azo I LB films. The three spectra are very similar to each other except for band intensities which increase almost linearly with increasing the number of monolayers, *n*, suggesting that structure of the LB films changes little as a function of *n* value. Bands due to CH_2 antisymmetric and symmetric stretching modes of the hydrocarbon chains are identified at 2923 and 2852 cm^{-1}, respectively. These frequencies indicate that the hydrocarbon chains of Azo I in the LB films are not fully in an ordered structure but include conformational disorder, *i.e. gauche* conformers to some extent [41]. A band at 1468 cm^{-1} is assignable to a CH_2 scissoring mode of the hydrocarbon chains, which is sensitive to the intermolecular interaction and thus often used to distinguish the lateral packings of the chains [42,43]; when the hydrocarbon chains crystallize with an orthorhombic subcell packing the band splits into two bands (~1473 and ~1463 cm^{-1}), whereas the splitting

does not take place when they are packed in a hexagonal or pseudohexagonal subcell [6,11,18]. The appearance of the singlet scissoring band shows that the hydrocarbon chains of Azo I in the LB films are in a hexagonal or analogous subcell packing.

The infrared transmission spectra of the LB films (Figure 3(A)) resemble that of the solid state (Figure 2(a)) except for relative intensities of some bands, but it should be noted that the band due to ClO_4^- observed strongly at 1090 cm^{-1} in the solid spectrum almost disappears in the LB film spectra. This observation indicates that most of ClO_4^- was lost during the formation of the LB films. The ClO_4^- band was observed strongly in the infrared spectrum of Azo I cast film which was prepared from its chloroform solution. Accordingly, it seems very likely that ClO_4^- was dissolved in the aqueous subphase when the chloroform solution was placed on it.

Infrared RA spectrum of the 10-monolayer Azo I LB film is shown in Figure 3(B). Comparison of band intensities in the infrared transmission and RA spectra of the 10-monolayer LB films enables us to discuss molecular orientation of the hydrocarbon chains and chromophore of Azo I. The intensities of the bands due to the CH_2 antisymmetric and symmetric stretching modes of the hydrocarbon chain are much stronger in the RA spectrum than in the transmission spectrum. According to surface selection rule [9,10,12,19], this result indicates that the hydrocarbon chains are tilted considerably with respect to the surface normal. The bands due to the in-plane vibrational modes of the

chromophoric part also gain intensities in the RA spectrum. However, it should be noted that the intensity enhancement of the 1516 cm^{-1} band due to the ν_{19}-like mode of the benzene ring is not so remarkable as that of the 1610 cm^{-1} band and the 843 cm^{-1} band arising from the CH out-of-plane mode of the benzene ring also gets intensity in the RA spectrum. These observations suggest that the benzothiazolium ring is fairly perpendicular to the substrate surface, but the benzene ring is tilted to some extent. Probably, Azo I molecule in the LB films is twisted in the C-N=N and/or N=N-C single bonds.

Polarized infrared transmission spectra of the 10-monolayer LB film of Azo I measured by using polarized infrared light with the electric vectors parallel and perpendicular to the direction of the dipping showed no significant dichroism for the infrared bands in the 4000-800 cm^{-1} region, indicating that the hydrocarbon chains in the Azo I LB films are uniaxially oriented with respect to the surface normal.

Infrared Spectra of Azo II LB Films

Figure 4(A) exhibits infrared transmission spectra of the 1-, 3-, and 9-monolayer Azo II LB films. The three spectra are again very similar to each other except for the band intensities, indicating that the structure of the LB films does not depend upon the number of monolayers. Bands due to the CH_2 antisymmetric and symmetric stretching modes of the hydrocarbon chains are observed at 2918 and 2849 cm^{-1}, respectively. These frequencies indicate that the Azo II LB films have highly ordered (*trans*-zigzag) hydrocarbon chains [41]. Probably, Azo II with two

hydrocarbon chains is more easily ordered in the LB films than Azo I with one hydrocarbon chain. A band arising from the CH_2 scissoring mode of the hydrocarbon chains is seen at 1470 cm^{-1}, suggesting that the hydrocarbon chains of Azo II in the LB films are in a hexagonal or analogous subcell packing. The band due to ClO_4^- is very weak in the LB film spectra, again indicating that most of ClO_4^- is removed in the course of LB film preparation.

Figure 4(B) presents infrared RA spectrum of the 9-monolayer Azo II LB film. Particularly striking in comparison between the infrared transmission and RA spectra of the 9-monolayer Azo II LB films is that the bands due to in-plane vibrational modes of the chromophore, in general, gain intensities greatly in the RA spectrum but the 1516 cm^{-1} band from the benzene ring does not show intensity enhancement and the 843 cm^{-1} band due to the CH out-of-plane mode of the benzene ring exhibits it significantly. These observations suggest that as in the case of Azo I the benzothiazolium ring of Azo II is fairly perpendicular to the surface in the LB films but its benzene ring is tilted considerably. The intensities of the bands due to the CH_2 antisymmetric and symmetric stretching modes do not show a remarkable change between the two spectra, indicating that the chains are neither perpendicular nor parallel to the surface, being in an intermediate direction.

The measurements of infrared polarized transmission spectra of the 9-monolayer Azo II LB film showed that the hydrocarbon chains in the LB film take an uniaxial orientation with respect to the surface normal.

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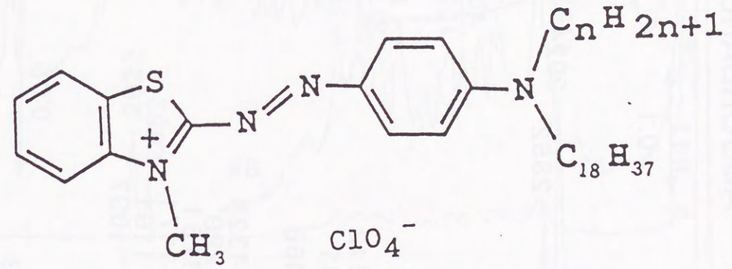

(n=2; Azo I)

(n=18; Azo II)

Figure 1. Structure of 2-(4'-ethyloctadecylaminophenylazo)-N-methylbenzothiazolium perchlorate (Azo I) and 2-(4'-dioctadecylaminophenylazo)-N-methylbenzo thiazolium perchlorate (Azo II).

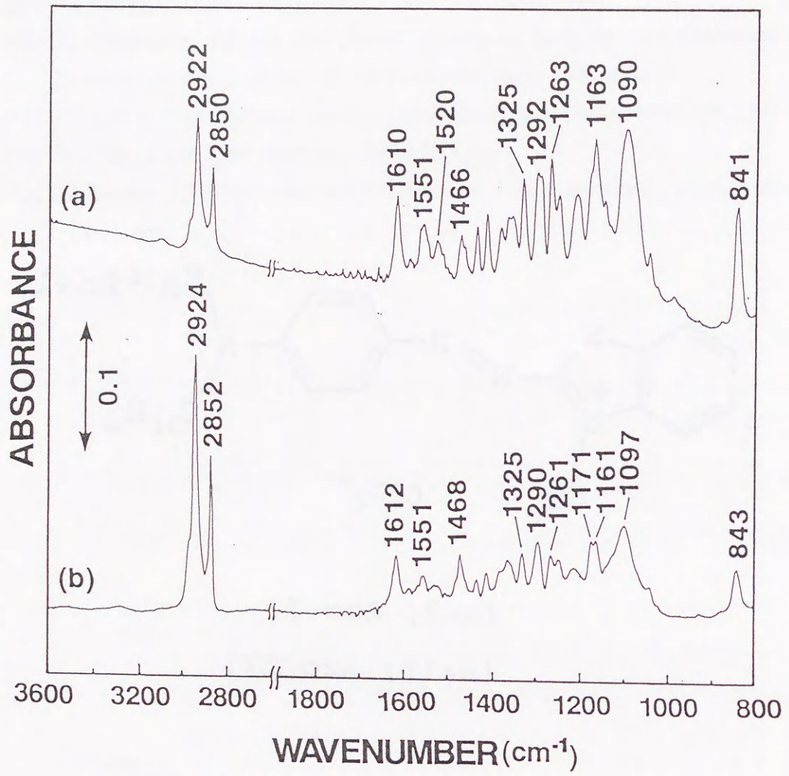

Figure 2. Infrared transmission spectra of Azo I (a) and Azo II (b) in solid states.

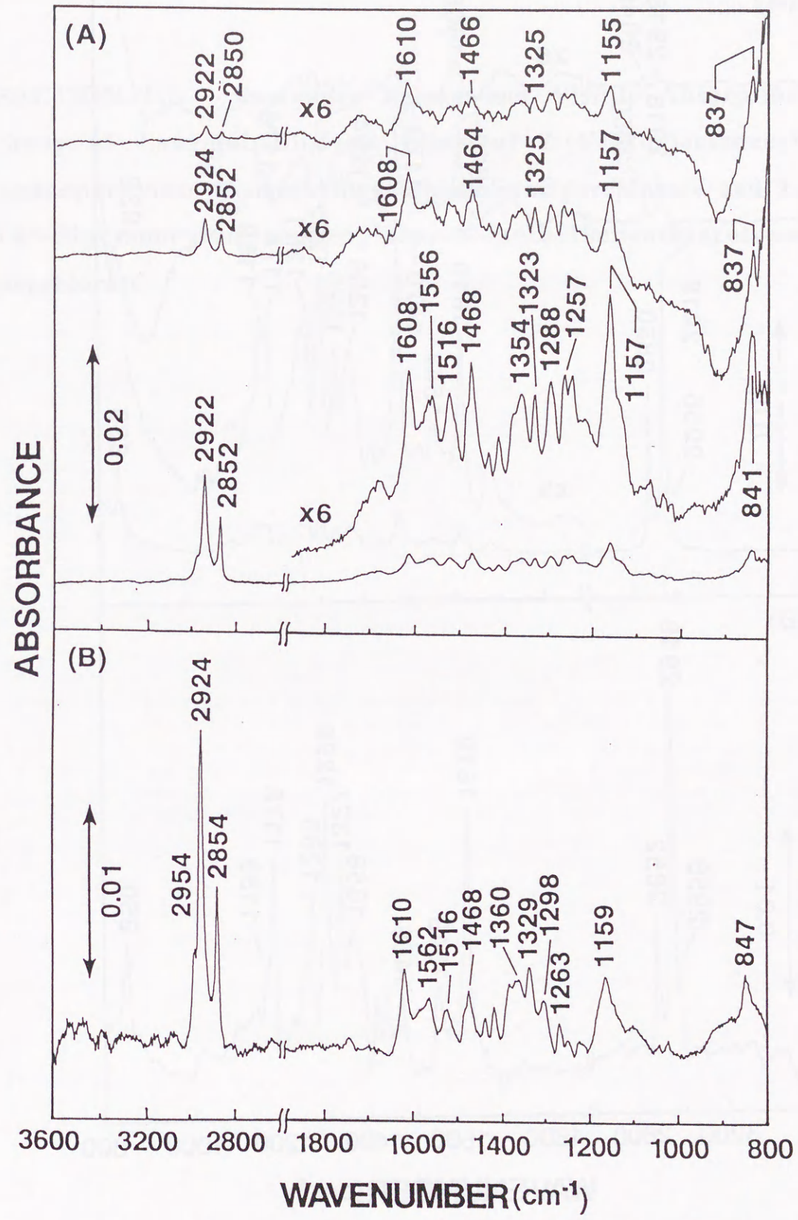

Figure 3. (A) Infrared transmission spectra of 2-, 4-, and 10-monolayer LB films of Azo I. (B) Infrared RA spectrum of 10-monolayer LB film of Azo I.

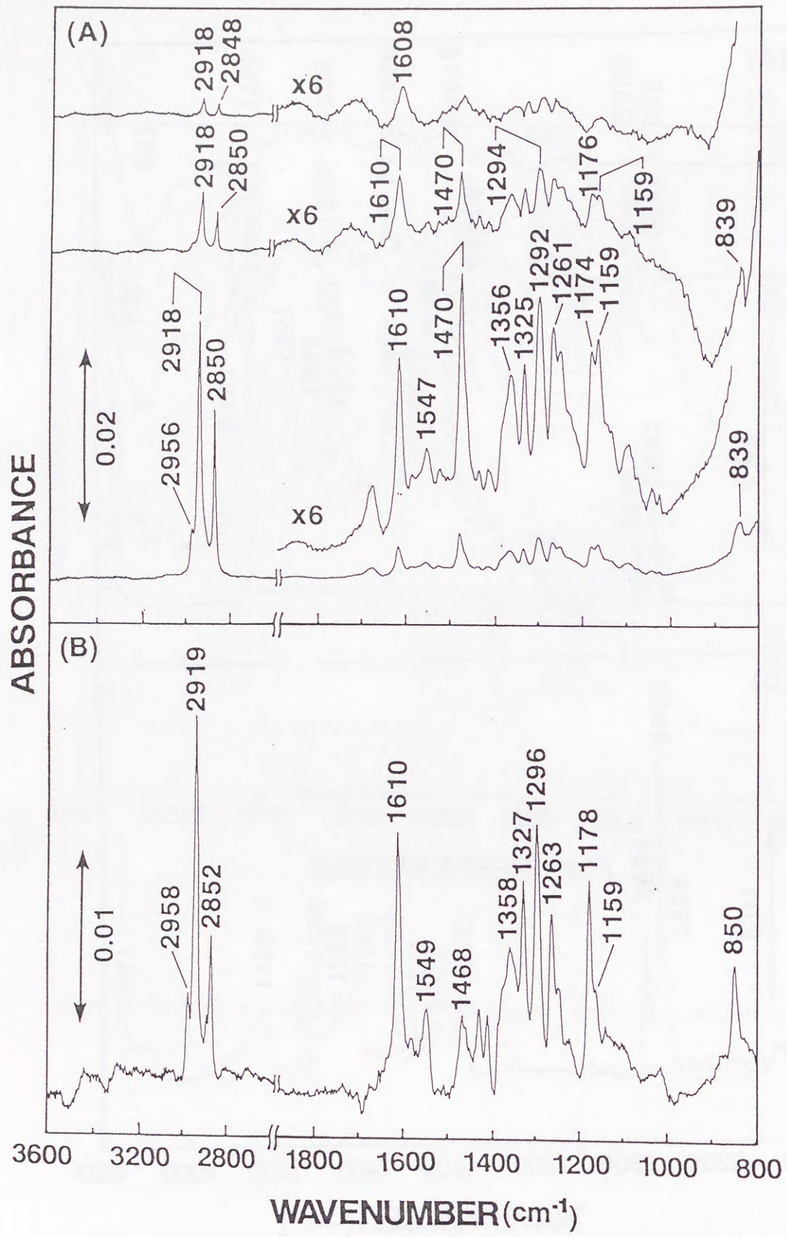

Figure 4. (A) Infrared transmission spectra of 1-, 3-, and 9-monolayer LB films of Azo II. (B) Infrared RA spectrum of 9-monolayer LB film of Azo II.

SECTION I-2: Resonance Raman and Visible Absorption Study of Langmuir-Blodgett Films of 2-(4'-Ethyloctadecyl aminophenylazo)-N-methylbenzothiazolium perchlorate and 2-(4'-Dioctadecylaminophenylazo)-N-methylbenzothiazolium perchlorate

ABSTRACT

Resonance Raman spectra of 1-, 3-, and 9-monolayer Langmuir-Blodgett (LB) films of 2-(4'-dioctadecylaminophenylazo) -N-methylbenzothiazolium perchlorate (Azo II) have been measured with high signal to noise ratio and compared with those of the dye in the cast film and solutions. A band assignable to the N=N stretching mode is observed at 1458 and 1465 cm^{-1}, respectively, in the LB film spectra and in the cast film and solution spectra. These observations suggest that Azo II takes a *trans* conformation around the -N=N- bond in the LB films as well as in the cast film and solutions but the conformation is slightly different between the LB films and the rest. Resonance Raman spectra of 2-(4'-ethyloctadecylaminophenylazo)-N-methylbenzothiazolium perchlorate (Azo I) in the 25-monolayers LB film, cast film and solutions are very similar to each other in contrast to the case of Azo II, indicating that the conformation and structure of the chromophoric part of Azo I change little among the three states. Visible absorption spectra of Azo I and Azo II LB films show that Azo II forms H-aggregates extensively in the films whereas Azo I does not form it.

INTRODUCTION

The study here has dual purposes. One is to present high quality resonance Raman spectrum of one monolayer LB film containing a chromophore. The other is to discuss structure of the chromophore in the LB films of 2-(4'-ethyloctadecylaminophenylazo)-N-methylbenzo thiazolium (Azo I, Figure 1) and 2-(4'-dioctadecylaminophenylazo) -N-methylbenzothiazolium (Azo II, Figure 1). Raman spectroscopy has recently been employed for studying the structure of LB films [1-14], but most of Raman studies of the LB films containing a functionally important chromophore have been performed by use of special techniques such as optical wave guide technique [1,3,6,9] and surface enhanced resonance Raman spectroscopy (SERRS) [2,4,5,7,14], and the studies by usual resonance Raman technique have been still rare. To our best knowledge, resonance Raman spectra of one monolayer LB films measured by usual resonance Raman technique with high signal to noise ratio have not been reported yet. Recently, unenhanced Raman spectra of one monolayer LB films of cadmium stearate were presented by two groups [10,13], but resonance Raman measurements of one monolayer LB film with a chromophore have different difficulty from that of unenhanced Raman measurements of one monolayer LB film without a chromophore. That is photo- and/or thermal-decomposition of the dye. Therefore, it is now very important to demonstrate one can measure high quality resonance Raman spectra of one monolayer LB film with a chromophore without any special techniques.

LB films of azo dyes have been a subject of keen interest because of their utility in photovoltaic cells and conducting, photochromic, and

nonlinear optical materials [15-19]. However, structure of the LB films of azo dyes has not been well investigated except for those of azobenzene-containing fatty acids [20,21]. Therefore, the present study, which treats new type of azo-containing LB films (LB films of Azo I and Azo II), may afford new insight into the structure of the LB films with an azo group.

EXPERIMENTAL

The samples of Azo I and Azo II were the same as those used in SECTION I-1. The preparations of LB films were described in previous section; CaF_2 and quartz plates were used as substrates.

Resonance Raman spectra were measured by using an apparatus consisting of a triple polychromator (SPEX 1877C), an intensified photodiode array detector (PAR 1455R-HQ) and a personal computer (NEC PC-9801 RA). The detector was used at -20 °C. The 488 nm and 514.5 nm lines from an Ar^+ laser (Spectra Physics 2016-05) was used for the excitation. The laser power at the sample position was 100-150 mW, and 8 cm^{-1} spectral slit width was employed. Frequency calibration was carried out by measuring Raman spectra of acetone and ethyl acetate, and estimated frequency errors were ± 2 cm^{-1}.

For measurements of the spectra of LB films an incidence angle of *ca.* 60° of laser line with respect to the surface normal was employed. Azo II gradually decomposed even with the illumination of a loosely focused laser beam. Therefore, each sample point of the LB films was illuminated by the laser beam only for 5 seconds, and to raise the signal to noise ratio of the spectrum the resonance Raman spectra were measured for 5 sampling points of each film and the obtained spectra were coadded. For the each measurement the exposure time and integration time were 1.0 second and 5 times, respectively. Stability of the LB films of Azo I against the laser illumination (488.0 nm, 100 mW) was much lower than that of Azo II, and therefore spectral quality of the resonance Raman spectra of Azo I was much worse than that of the

resonance Raman spectra of Azo II.

The dye seemed to be stable in methylene chloride, chloroform, and acetone solutions; resonance Raman spectra of the solutions did not change with time. The exposure time and integration time were 0.3 second and 50 times, respectively.

The data calculations were performed on CORASS (Rikei Co. Ltd.) and self-made programs.

Absorption spectra were recorded on a Shimadzu UV-360 spectrophotometer.

RESULTS AND DISCUSSION

Visible absorption Spectra of Azo I and Azo II

It is very important to study visible absorption spectra to know aggregation states of dye molecules in the LB films and to analyze their resonance Raman spectra. Figure 2 compares the absorption spectra of Azo I in the 10-monolayer LB (a) and cast films (b) and the acetone solution (c). The spectra of Azo I solution and LB film show two absorption maxima near 600 and 560 nm assignable to the monomer and dimer, respectively, while the cast film spectrum gives the third absorption maximum at 480 nm. On the analogy of absorption spectra of azobenzene [20] and cyanine dyes [23], it may be considered that blue shifted band of the cast film arises from H-aggregates of Azo I.

Figure 3 exhibits absorption spectra of the LB (a) and cast films (b) and acetone solution (c) of Azo II. The spectra of chloroform (λ_{max}= 598 nm) and methylene chloride (λ_{max}= 604 nm) solutions are very similar to that of the acetone solution. The three spectra in Figure 3 are markedly different from each other, and particularly notable are appearances of blue shifted bands assignable to H-aggregates in the LB (λ_{max}= 488 nm) and cast film (λ_{max}= 446 nm) spectra. Probably, the LB and cast films form different types of H-aggregates. The 488.0-nm excitation of Raman spectra of the LB and cast films of Azo II yields predominantly resonance Raman spectra of their H-aggregates.

The absorption spectrum of the Azo I LB film is largely different from that of the Azo II one; the latter gives an intense band due to H-aggregates but the former does not show a band assignable to it (Figure 2(a) and 3(a)). It is particularly notable that Azo II forms H-aggregates

extensively in the LB films but Azo I does not form it. There is little doubt that the difference in the number of the hydrocarbon chain causes a crucial change of the aggregation state in the LB films. The absorption spectrum of Azo I cast film is also clearly different from that of Azo II cast film. The former shows a band at 480 nm ascribed to H-aggregate while the latter provides it at 446 nm, indicating that different kinds of H-aggregate are formed in the Azo I and Azo II cast films.

Resonance Raman Spectra of Azo II

The 488.0-nm excited resonance Raman spectra of the 1-(a), 3-(b), and 9-(c) monolayer LB films of Azo II are shown in Figure 4, where the spectrum of its cast film (d) is also presented for comparison purpose. Spectral quality of the single monolayer spectrum is very high, and thus one can discuss the structure of the dye in the single monolayer LB film. The 514.5-nm excitation provided similar spectra to those in Figure 4, but the background due to fluorescence became stronger there.

The three LB film spectra (a-c) are very similar to each other. Therefore, it is considered that the structure of the dye does not depend upon the number of monolayers and the interaction between the dye and the substrate is very weak.

Vibrational assignments of the spectra in Figure 4 are not straightforward, but it may be possible to make a tentative assignment for several bands by referring to Raman spectra of benzene and azobenzene derivatives for which vibrational assignments have been well established [24-28]. An intense band at 1611 cm^{-1} seems to be due to a $^{+}N=C$ stretching mode of the benzothiazolium ring because unsaturated amine

salts give an intense band due to a $^{+}N=C$ stretching mode in the 1700-1620 cm^{-1} region [29] while azobenzene derivatives [26-28] and thiacarbocyanines [30], which have the benzothiazolium ring with a N-C bond, yield only weak to medium features near 1600 cm^{-1}. A medium band near 1520 cm^{-1} may be assigned to ν_{19} like mode of the benzene ring. Bands at 1459 and near 1178 cm^{-1} are assignable to -N=N- and =N-Ph stretching modes, respectively, on the analogy of those of azobenzene derivatives [24-28].

The $^{+}N=C$ stretching frequency of Azo II in the LB films is appreciably lower than usual and its ν_{19} frequency is somewhat higher than usual. These results suggest that resonance structure (b) in Figure 1 makes a significant contribution to the true structure. It is well known that the -N=N- stretching frequency of azobenzene derivatives is very sensitive to conformation around the -N=N- group; a *trans* conformer gives the -N=N- stretching mode near 1430 cm^{-1} while a *cis* conformer provides it near 1510 cm^{-1} [24-28]. Judging from structural difference between azobenzene derivatives and Azo II, it seems reasonable to assume that vibrational frequencies of the N=N stretching bands of *trans* and *cis* isomers of Azo II are considerably higher than those of azobenzene derivatives. Therefore, the observations in Figure 4 indicate that Azo II assumes a *trans* conformer in the LB films.

The resonance Raman spectrum of the cast film (Figure 4(d)) resembles those of the LB films (Figure 4(a-c)), but it is noted that there are significant differences in the vibrational frequency of the -N=N-

mode and in spectral pattern in the 1350-1150 cm^{-1} region between the cast and LB film spectra; the band due to the -N=N- stretching mode shows an upward shift by *ca.* 6 cm^{-1} in the former. The N=N stretching frequency is, in general, sensitive to a change in the contribution of resonance structure like Figure 1(b) and that in conformation about the -N=N- linkage [26-28]. However, it seems very unlikely in the above case that the change in the contribution of resonance structure causes the shift since the frequency of the $^{+}$N=C stretching band alters little between the LB film spectra and the cast film one. Twisting in the C-N=N or N=N-Ph single bond is also unlikely because it would bring about a band shift not only in the -N=N- stretching mode but also in the $^{+}$N=C or C=C stretching mode of the benzene ring. Therefore, it may be considered that slight alterations in C-N=N and/or N=N-Ph angles cause the frequency shift of the -N=N- stretching band.

The differences in the spectral pattern in the 1350-1150 cm^{-1} region between the LB and cast film spectra may arise from resonance Raman effect because resonance Raman spectra in the above region of the LB films become close to that of the cast film with the 514.5-nm excitation.

Figure 5 presents the 514.5-nm excited resonance Raman spectra of Azo II in acetone (a), chloroform (b), and methylene chloride (c) solutions. The 488.0-nm excitation did not yield good spectra probably because it is out of resonance condition (see absorption spectrum of Azo II acetone solution in Figure 3). The three spectra are very similar to each other, indicating that the contribution of resonance structure (Figure 1(b)) alters little with solvents irrespective of the difference of their

polarity. Probably, the interactions between the dye and solvents are very weak. The N=N stretching bands of the solution spectra are observed near 1464 cm^{-1}. These observations suggest that the dye assumes a *trans* conformer in the solutions and the conformation around the -N=N- bond there is closer to that in the cast film than that in the LB films.

Resonance Raman Spectra of Azo I

Figure 6 presents the 514.5-nm excited resonance Raman spectra of Azo I in acetone (a), chloroform (b), and methylene chloride (c) solutions. The 514.5-nm excitation is closer to the dimer absorption of Azo I solutions, and therefore yields predominantly resonance Raman spectra of the dimer. The spectra of the three solutions are very close to each other. This result indicates that the contribution of resonance structure alters little with solvents irrespective of the difference of their polarities and the interactions between the dye and solvents are very weak.

As in the case of resonance Raman spectra of Azo II solutions, bands at 1612, 1520, and 1463 cm^{-1} can be assigned to a $^{+}$N=C stretching mode, ν_{19} mode of the benzene ring, and N=N stretching mode, respectively. A band at 1160 cm^{-1}, which seems to correspond to the infrared band at 1163 cm^{-1} of Azo I in the solid state, may be due to a =N-Ph stretching mode. The appearances of N=N and =N-Ph stretching modes at 1463 and 1160 cm^{-1}, respectively, show that the Azo I dimer assumes a *trans* conformation around the N=N bond in the solutions [25-28].

The 514.5-nm excited resonance Raman spectra of the 25-monolayer LB (a) and cast films (b) of Azo I are shown in Figure 7. The 514.5-nm excitation provides chiefly resonance Raman spectrum of the dimer for the LB film because it is close to its dimer absorption maximum (Figure 2 (a)) while the same excitation enhances both resonance Raman spectrum of the dimer and that of H-aggregate for the cast film. The 488.0-nm excited resonance Raman spectrum of the cast film, which mainly consists of spectrum of the H-aggregate, is almost identical with that of the 514.5-nm excited resonance Raman spectrum of the cast film. Therefore, it seems that the resonance Raman spectra of the dimer and H-aggregate of the cast film are nearly the same.

Vibrational frequencies of bands due to the $^{+}$N=C stretching mode, ν_{19}-like mode of the benzene ring, N=N stretching mode, and =N-Ph stretching mode change little among the spectra of the LB and cast films and solutions. This result leads to consider that at least as far as the dimer is concerned, the conformation and electronic structure of Azo I does not change appreciably among the LB and cast films and solutions. In this regard the different conclusion was obtained for Azo II H-aggregates as described above; conformation around the -N=N- bond alters slightly between the LB and cast films of Azo II H-aggregates.

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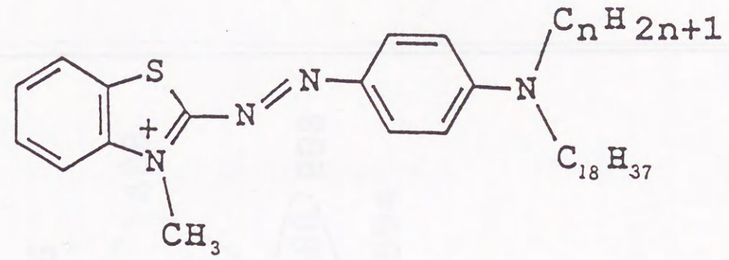
(a)



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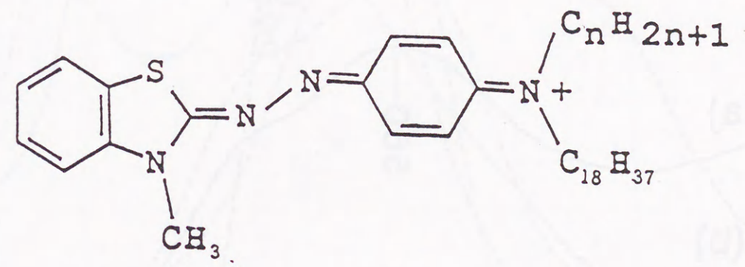

(n=2; Azo I)

(n=18; Azo II)

Figure 1. Structure of 2-(4'-ethyloctadecylaminophenylazo)-N-methylbenzothiazolium perchlorate (Azo I) and 2-(4'-dioctadecylaminophenylazo)-N-methylbenzo thiazolium perchlorate (Azo II) (a) and their resonance structure (b).

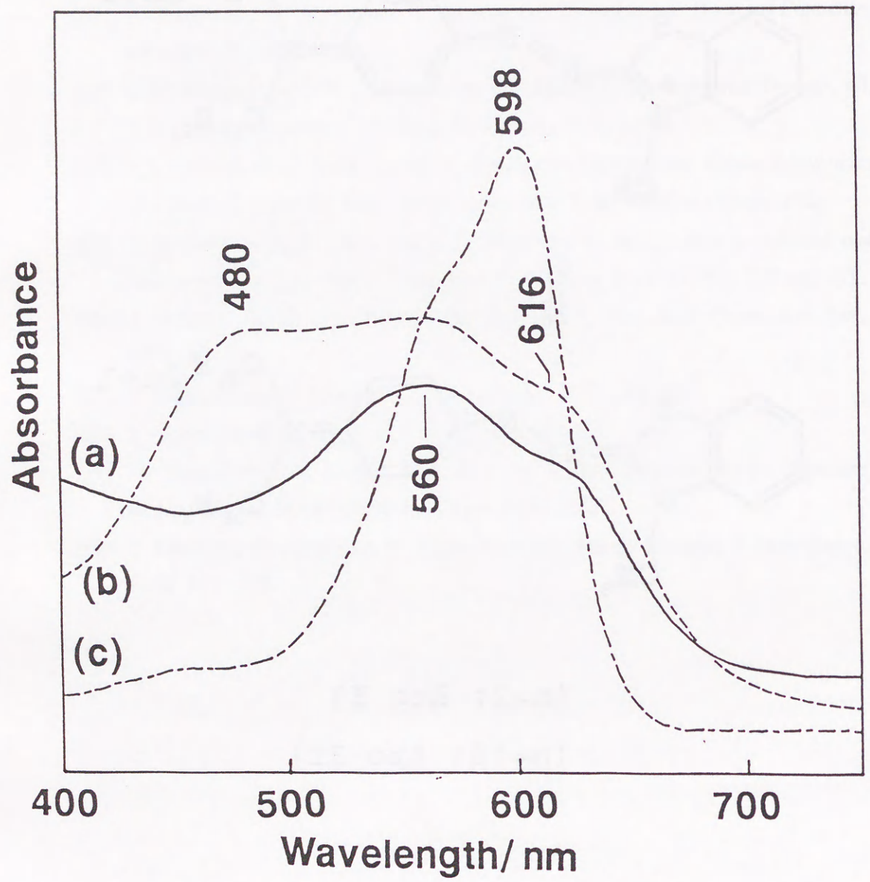

Figure 2. Visible absorption spectra of 10-monolayer LB film (a), cast film (b), and acetone solution (c) of Azo I.

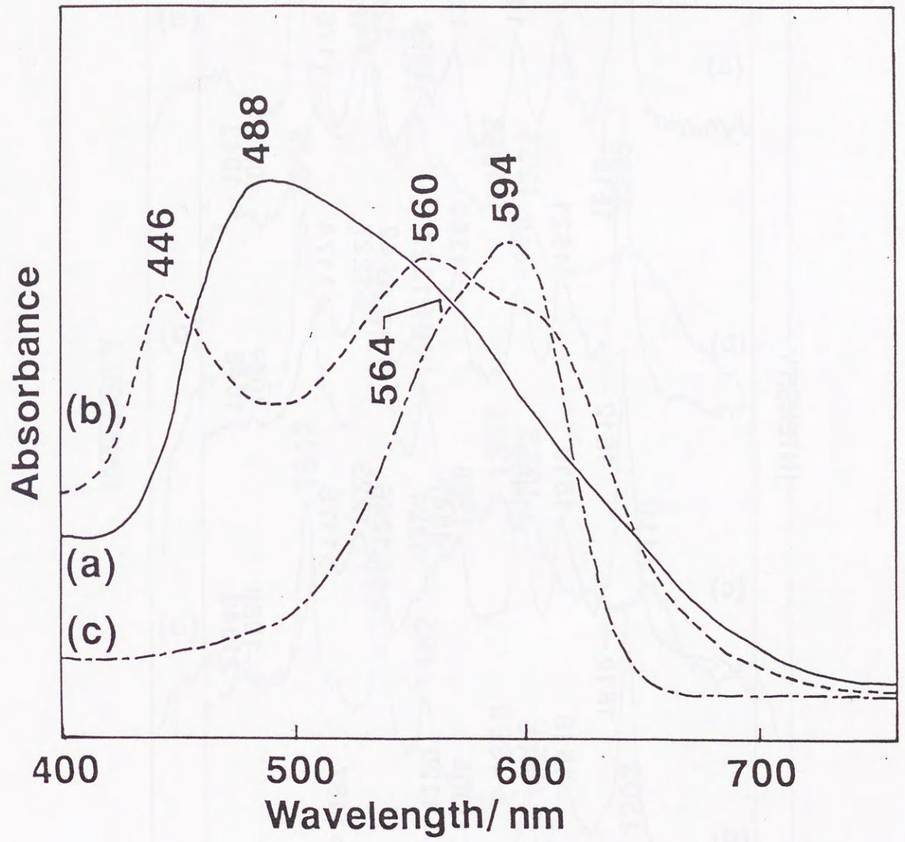

Figure 3. Visible absorption spectra of the 9-monolayer LB film (a), cast film (b), and acetone solution (c) of Azo II.

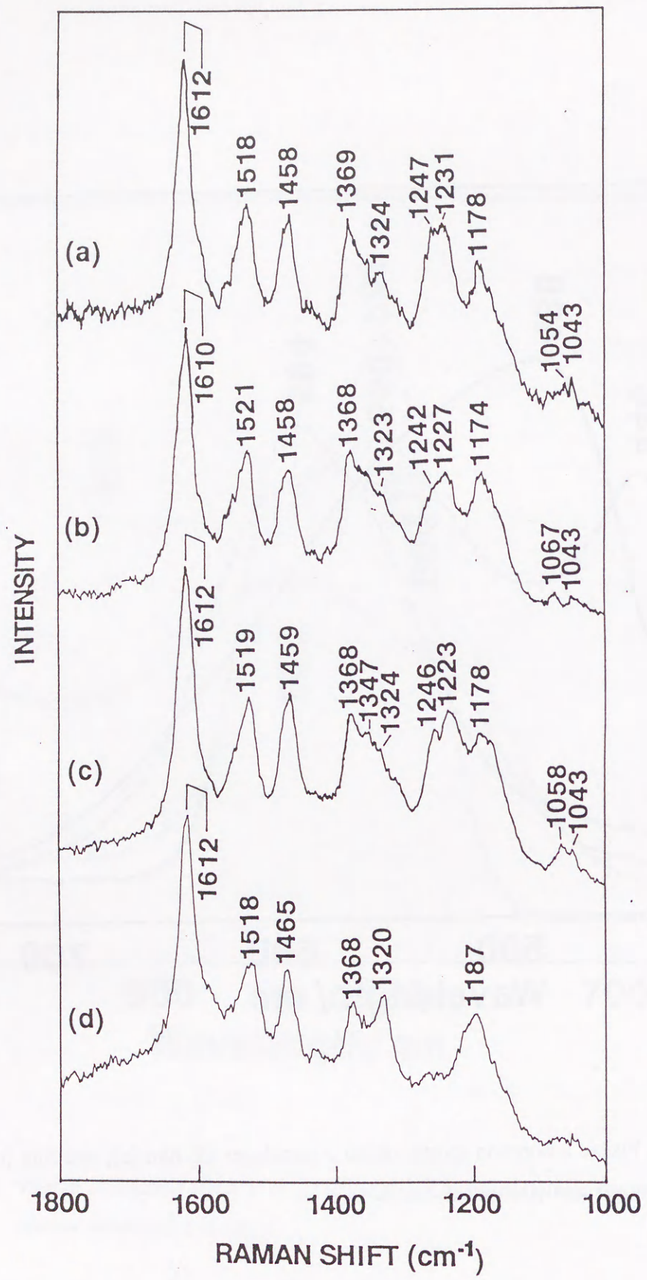

Figure 4. The 488.0-nm excited resonance Raman spectra of the 1-(a), 3-(b), and 9-(c) monolayer LB and cast (d) films of Azo II.

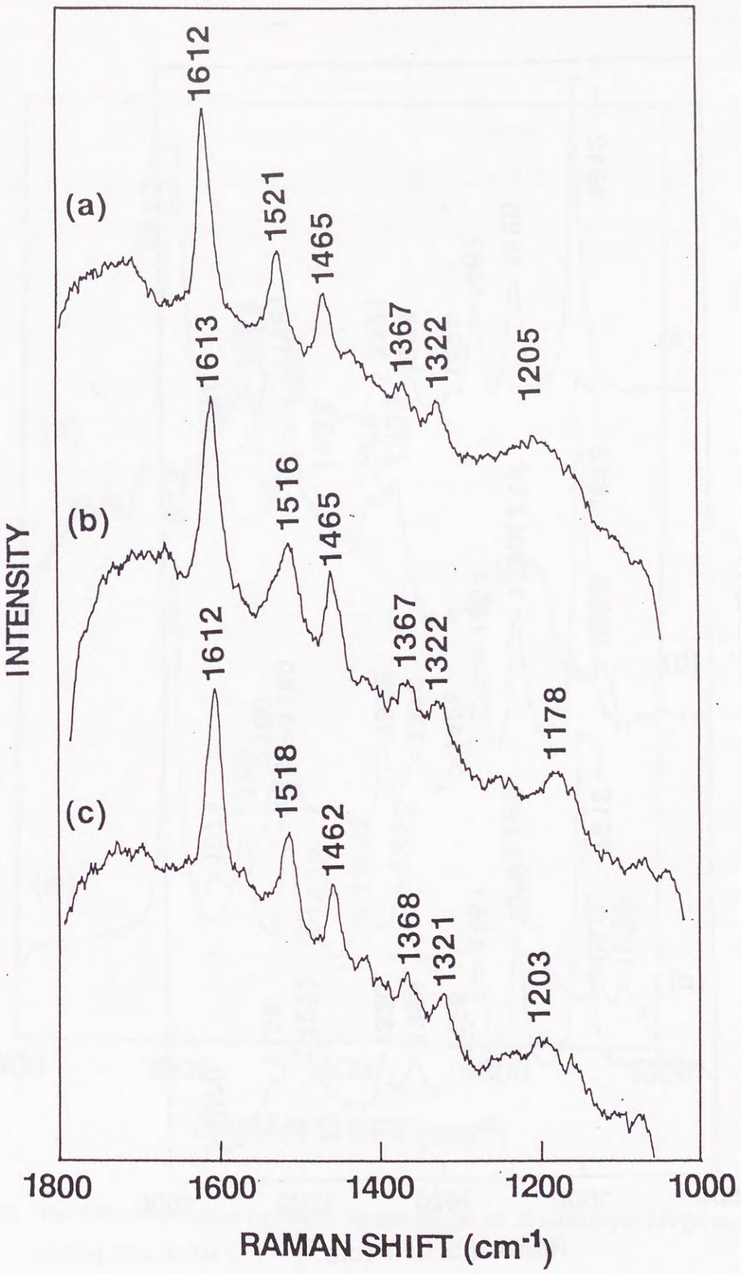

Figure 5. The 514.5-nm excited resonance Raman spectra of Azo II in acetone (a), chloroform (b), and methylene chloride (c) solutions.

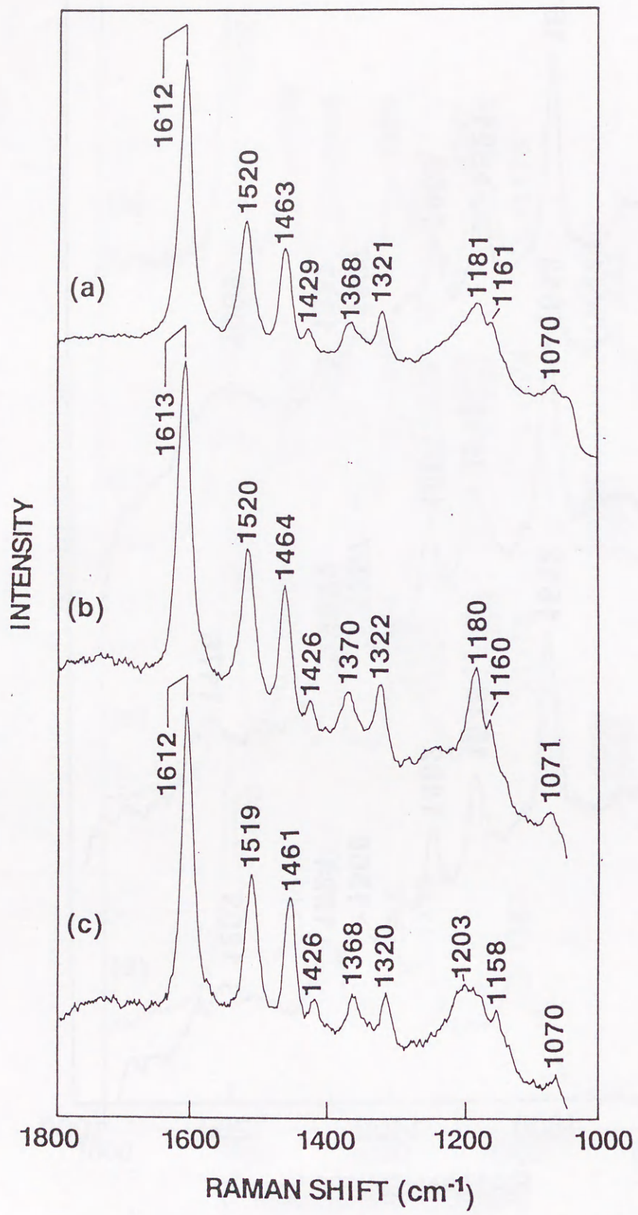

Figure 6. The 514.5-nm excited resonance Raman spectra of Azo I in acetone (a), chloroform (b), and methylene chloride (c) solutions.

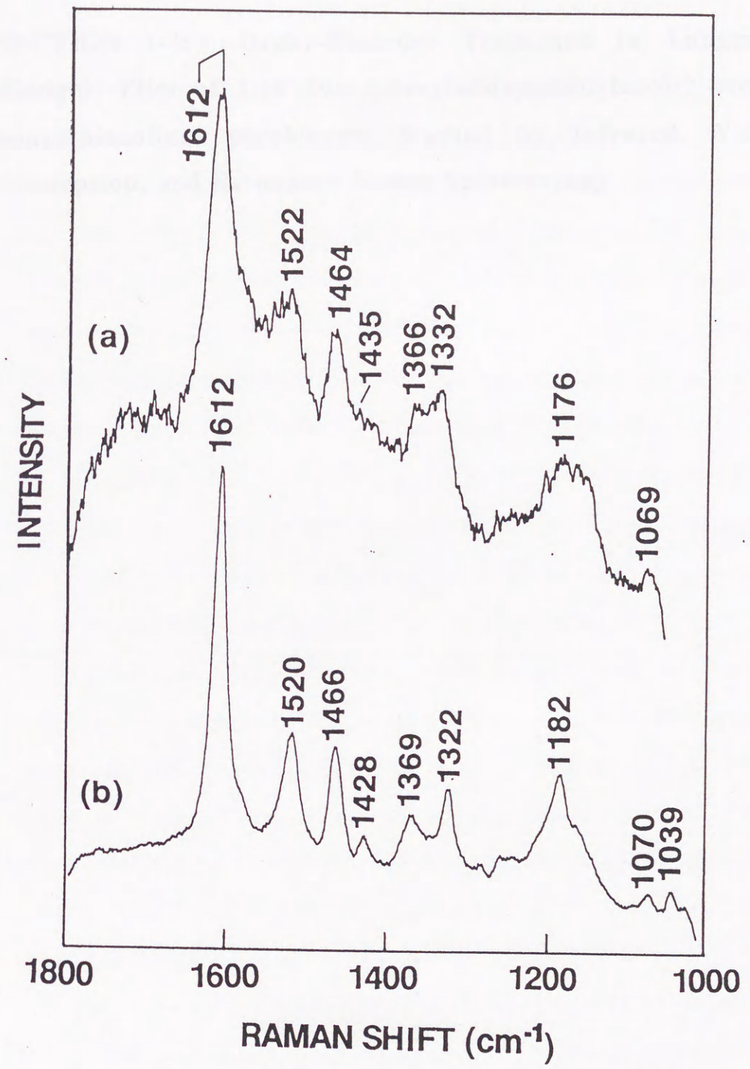

Figure 7. The 488.0-nm excited resonance Raman spectra of 25-monolayer LB (a) and cast (b) films of Azo I.

SECTION I-3: Order-Disorder Transition in Langmuir-Blodgett Film of 2-(4'-Dioctadecylaminophenylazo)-N-methyl benzothiazolium perchlorate Studied by Infrared, Visible Absorption, and Resonance Raman Spectroscopy

ABSTRACT

Infrared transmission, visible absorption, and resonance Raman spectra of 15-monolayer Langmuir-Blodgett (LB) films of 2-(4'-(dioctadecylamino)phenylazo)-N-methylbenzothiazolium perchlorate (Azo II; Figure 1) have been measured at elevated temperatures, and order-disorder transition of the films has been investigated. Upward shifts of CH_2 antisymmetric and symmetric stretching bands of the hydrocarbon chains suggest that the order-disorder transition of the tail groups occurs around 70 °C in the films. Prior to the transition the two CH_2 stretching bands show broadening (50 ~ 70 °C), indicating that the alkyl chain mobility begins to increase before their conformational disorder occurs. The visible absorption and resonance Raman spectra of the LB films of Azo II undergo marked changes in the same temperature range as the infrared bands due to the CH_2 stretching modes show the broadening. The spectral changes in the visible absorption and resonance Raman spectra are indicative of the conversion from an H-aggregate to monomers in the chromophoric part of Azo II, and therefore, it seems likely that the conversion is linked with the increase in the mobility of the hydrocarbon chains. Cyclic thermal treatment experiments in the infrared spectra of the Azo II LB film show that not only bands due to the chromophoric part but also the CH_2 stretching bands do not return to original spectral features after cycling the temperature to 70 °C. This result indicates that the orientation and/or aggregation in the head groups do not recover upon the cyclic thermal treatment to 70 °C and the remaining disorder in the head groups hinders reversible order-disorder transition in the alkyl tails.

INTRODUCTION

Order-disorder transitions in Langmuir-Blodgett (LB) films have been a matter of keen interest from following standpoints [1,2]. One is that the order-disorder transitions in LB films show various characteristics different from those of bulk hydrocarbon materials; LB monolayers may be an example of a system exhibiting two-dimensional phase transitions and melting [2-4]. The other is that the studies on the order-disorder transitions are practically important because the transitions are deeply concerned with the thermal stability of LB films [1,2]. Yet another is that the studies are very useful in understanding the nature of phase transitions of biologically-relevant membranes such as lipid bilayers.

In spite of the importance of the studies, however, the structural characterization of LB films at elevated temperatures had been virtually nonexistent until 1985 probably because the lack of a powerful structural probe. In 1985, Naselli *et al.* [4,5] reported the first detailed study on the order-disorder transition in a LB film of cadmium arachidate by using infrared reflection-absorption (RA) spectroscopy. They observed a two-step melting process in the LB film; in the first step a pretransitional disordering of the alkyl tails occurred below the melting point, and this was followed by an irreversible breakup of the head group above the melting point [4]. After their reports a few groups presented infrared investigations on order-disorder transitions of LB films [6-9]. For example, Cohen *et al.* [6] compared the thermal stability of a LB film of cadmium arachidate on aluminum oxide with that of a LB film of cadmium arachidate on a n-octadecyltrichlorosilane (OTS) monolayer.

However, they all treated LB films consisting of very simple compounds such as cadmium arachidate expect for one exception, where temperature dependencies of infrared spectra of LB films of a polydiacetylene derivative were reported, but the detailed analysis of these spectra was not presented [9].

Raman spectroscopy has been also employed for investigating the order-disorder transitions of LB films [3,10-14]. Again, so far, there has been no report dealing with LB film containing an organic dye.

The study here has dual purposes. One is to report an infrared and resonance Raman study on the phase transition of LB film having a large chromophoric part for the first time and to compare its order-disorder transition with those of LB films without a large chromophoric part. The other is to provide further insight into the thermal stability of the LB film with a large chromophoric part. I treat here LB films of 2-(4'-dioctadecylamino)phenylazo)-N-methylbenzothiazolium perchlorate (Azo II; Figure 1) for which I already carried out structural characterization at room temperature by using infrared, visible absorption, and resonance Raman spectroscopy as described in previous sections of this part.

EXPERIMENTAL

Azo II sample used in this experiment is the same as that reported previously [15,16]. The melting point of Azo II determined by a Yanaco micro melting point apparatus was 110 °C and the dye was thermally stable until this temperature. The Y-type 15-monolayer LB films of Azo II were prepared by the method described previously [15,16]. For infrared transmission and visible absorption, and resonance Raman measurements the LB films were deposited on CaF_2 and quartz plates, respectively.

A cast film of Azo II was prepared from a chloroform solution on a CaF_2 plate.

The instrumentations and sample-handling techniques adopted in this work for recording the infrared, visible absorption, and resonance Raman spectra were the same as those described previously [15,16]. In order to raise the LB films to elevated temperatures, a copper block device having a ceramic heater within was designed. The CaF_2 plate on which the LB film had been deposited was inserted into a sample holder in the block and temperature was controlled by using an Omron E5T program thermocontroller which gave a temperature stability of better than ± 0.1 °C. The temperature was monitored with a thermocouple connected with the sample holder and was raised at *ca.* 1.0 °Cmin^{-1}. Bandwidths in the infrared spectra were obtained by computing the widths at 1/2 of the peak height. The precision and reproducibility of measuring temperature-induced changes in infrared frequency and bandwidth is better than ± 0.05 cm^{-1}.

Differential scanning calorimetry (DSC) measurement of Azo II in a powdered state was carried out with a Seiko Instruments SSC 5000 using a heating rate of 2 °C min^{-1}.

RESULTS

Figure 2 exhibits visible absorption spectra of the 15-monolayer LB film of Azo II as a function of temperature. In our previous study bands near 490, 560, and 620 nm were assigned to H-aggregate, dimer, and monomer of Azo II, respectively [15,16]. It can be seen in Figure 2 that in the range of 50 to 75 °C temperature increase results in an intensity decrease in the band due to the H-aggregate and an intensity increase in the monomer peak. Probably, the H-aggregate is broken into the monomers. Above 80 °C, the intensities of all the bands decrease gradually, indicating partial thermal decomposition of the dye.

We also examined cyclic thermal treatments for the LB film of Azo II by using absorption spectroscopy. First, temperature of the sample was raised to 70 °C, its spectrum recorded, then lowered to 30 °C, and the subsequent spectrum obtained. The subsequent spectrum was much closer to the spectrum measured at 70 °C than the original spectrum, suggesting that the conversion from the H-aggregate to the monomers is largely irreversible.

Infrared transmission spectra of the 15-monolayer LB film of Azo II recorded at 30(a), 50(b), 70(c), 90(d), 110(e), and 140(f) °C are shown in Figure 3. Intense bands at 2918 and 2850 cm^{-1} in Figure 3 (a) are assigned to CH_2 antisymmetric and symmetric stretching modes of the alkyl tails. It is well known that the frequencies and bandwidths of CH_2 antisymmetric and symmetric stretching bands are sensitive to the conformation and mobility of hydrocarbon chain, respectively [17-19]. The bands at 2918 and 2850 cm^{-1} show considerable broadening as well

as high-frequency shifts at elevated temperatures.

Figure 4 (a) and (b) illustrate temperature dependencies of the frequencies and bandwidths of the CH_2 antisymmetric and symmetric stretching bands, respectively. Of particular note is that the frequencies show remarkable changes between 60 and 80 °C while the bandwidths demonstrate clear alterations between 50 and 70 °C.

According to our previous paper [16], bands at 1608, 1581, 1514, 1470, and 1159 cm^{-1} in the spectrum of Figure 3(a) are assigned to a $^{+}N=C$ stretching mode, ν_8 and ν_{19} modes of the benzene ring, CH_2 scissoring mode of the hydrocarbon chains, and =N-Ph stretching mode, respectively. The CH_2 scissoring band becomes broad above 50 °C as in the cases of the CH_2 symmetric and antisymmetric stretching bands. Frequencies and band shapes of the $^{+}N=C$ stretching, ν_8, ν_{19}, and =N-Ph stretching bands are unchanged between 30 and 50 °C. However, significant changes are observed in the spectrum recorded at 70 °C; *i.e.* the intensities of the ν_8 and ν_{19} bands increase while those of the bands in the 1350-1240 cm^{-1} region decrease appreciably (compare the intensity ratio of two bands at 1288 and 1157 cm^{-1} in Figure 3 (b) and (c)). The observed changes are probably related with the changes seen in the visible spectra in Figure 2. It seems likely that the conversion from the H-aggregate to the monomers causes the above-mentioned intensity changes in the infrared bands.

At the first glance the two spectra recorded at 50 and 70 °C looked very close to each other, but it has turned out from the cyclic thermal

experiments that the spectral differences they show are small but very important. As the temperature is raised from 70 to 90 °C broadening of the bands below 1650 cm^{-1} becomes remarkable and a downward shift of the $^{+}N=C$ stretching band is also noted. It should be notable that the spectral changes observed between 50 and 70 °C do not include a band shift but those seen between 70 and 90 °C consist of the band shifts (see, 1607, 1512, 1356 and 1244 cm^{-1} bands) and broadening. It is probable that the spectral alterations between 50 and 70 °C correspond to the conversion from the H-aggregate to the monomers and those between 70 and 90 °C include not only the changes due to the conversion but also those attributed to the thermal decomposition. Above 90 °C the bands below 1650 cm^{-1} become very broad and lose their features.

Figure 5 illustrates infrared spectral changes for the 15-monolayer LB film of Azo II subjected to cyclic thermal treatments. First, temperature of the sample was raised to 50 °C, its spectrum recorded (Figure 5(b)), then lowered to 30 °C, and the subsequent spectrum obtained (Figure 5(c)). The latter spectrum was almost identical with the original one shown in Figure 5(a). Then, the temperature was raised to 70 °C. After measuring the spectrum at 70 °C (Figure 5(d)) it was recorded at 30 °C (Figure 5(e)). Cycling the temperature to 70 °C resulted in the spectrum (Figure 5(e)) which is much closer to Figure 5(d) than Figure 5(a) (see, for example, the frequencies and bandwidths of the CH_2 stretching bands and spectral features in the 1610-1450 cm^{-1} region). The last observation is in good agreement with that for the visible absorption spectra.

Figure 6 presents the 488.0-nm excited resonance Raman spectra of the 15-monolayer LB film of Azo II recorded at 30(a), 50(b), 70(c), and 90(d) °C. In our previous paper bands at 1612, 1520, and 1460 cm^{-1} were assigned to a $^{+}N=C$ stretching, ν_{19}, and N=N stretching modes, respectively [15]. Vibrational frequencies and intensities of bands in Figure 6(a) and (b) are almost identical with those in the spectra of the LB films of Azo II previously reported [15]. As the temperature is increased from 50 to 70 °C, the N=N stretching band shows a high-frequency shift to 1465 cm^{-1} and the relative intensity of a band at 1230 cm^{-1} decreases; the spectrum of the LB film becomes close to those of the cast film and solutions of Azo II [15].

The signal to noise ratio of the Raman spectrum is rather poor at 90 °C because the strong resonance Raman effect can not be expected due to the weak absorbance at 90 °C.

In Figure 7 (a) and (b) are illustrated temperature dependencies of the frequencies and bandwidths of the CH_2 antisymmetric and symmetric stretching bands of a cast film of Azo II, respectively. The frequencies of the cast film show marked changes at much lower temperature than those of the LB film (Figure 4 (a) and Figure 7 (a)) and the bandwidths of the former do not demonstrate clear transitions.

DISCUSSION

Molecular aggregation, orientation, and structure in LB films of Azo II were investigated in some detail in our previous papers by using infrared, visible absorption, and resonance Raman spectroscopies [15,16]. Following conclusions could be reached as to them [15,16]. (i) The chromophoric part of Azo II forms different kinds of H-aggregates in the LB and cast films. (ii) It takes a *trans* conformation around the -N=N- bond in the LB films as well as in the cast film and solutions but the conformation is slightly different in the N=N bond moiety between the LB films and the rest. (iii) The benzothiazolium ring of Azo II is fairly perpendicular to the substrate surface but its benzene ring is tilted appreciably. (iv) The hydrocarbon chains of Azo II, which are highly ordered (*trans*-zigzag), are neither perpendicular nor parallel to the substrate surface, being tilted with respect to the surface normal. These structural information provides a basis for investigating the order-disorder transition of Azo II LB films.

Order-disorder Transition in the 15-monolayer Langmuir-Blodgett Film of Azo II

The frequencies of the CH_2 antisymmetric and symmetric stretching bands have been used as practical indicators of order-disorder transitions of hydrocarbon chains because they are very sensitive to the degree of their conformational order [17-19]. When the chains are highly ordered (*trans*-zigzag conformation), the bands appear near 2918 and 2850 cm^{-1}, respectively, while if conformational disorder is included in the chains,

they shift upward up to near 2927 and 2856 cm^{-1} depending upon the content of *gauche* conformers. Therefore, the results in Figure 4(a) show that the hydrocarbon chains in the LB film of Azo II begin to be disordered around 60 °C and above 80 °C they are in highly disordered conditions. It can be seen from Figure 4(a) that the hydrocarbon chains have phase transition point at about 70 °C. It should be noted that prior to the point there observes the broadening of the bandwidths of the CH_2 antisymmetric and symmetric stretching bands (Figure 4(b)). The changes in the frequencies and bandwidths are not always concerted. Since it is well known that the increased bandwidths result from an increase in the mobility of an alkyl chain, the observations in Figure 4(b) indicate that the alkyl chain mobility begins to increase prior to the conformational changes in the hydrocarbon chains. This sort of behavior of the chains has already been observed for phospholipids [20,21] and ascorbyl palmitate [17].

The temperature range where the alkyl chain mobility increases is almost identical with that where the conversion from the H-aggregate to the monomers of Azo II occurs. Therefore, it seems that the increase in the alkyl chain mobility causes the conversion.

The relative intensity changes in the bands at 1581 and 1514 cm^{-1} and those in the 1400-1200 cm^{-1} region observed between 50 and 70 °C (Figure 3(b) and (c)) are probably in parallel with the alterations in the bandwidths of the CH_2 stretching bands (Figure 4(b)). Accordingly, it may be concluded that the above-mentioned intensity changes reflect the conversion from the H-aggregate to the monomers brought about by the

increased mobility of the hydrocarbon tails. The intensity increases in the bands at 1581 and 1514 cm^{-1} and the decreases in those in the 1400-1200 cm^{-1} region between 50 and 90 °C suggest that the orientation of chromophoric part is lost during the conversion.

The resonance Raman spectra of the LB film of Azo II also show marked changes attributed to the conversion from the H-aggregate to the monomers in the temperature range where the hydrocarbon chains gain their mobility (Figure 4(b) and Figure 6(b) and 6(c)).

In the previous section it was found that the resonance Raman spectrum of the cast film of Azo II and those of its solutions are very close to each other but the spectra of the LB films are significantly different from them in the frequency of the N=N stretching band and the band contour in the 1250-1150 cm^{-1} region [15]. Figure 6 demonstrates that as the temperature is raised from 50 to 70 °C the resonance Raman spectrum of the Azo II LB film undergoes a conversion from one type which is almost identical with the previously reported spectra of the LB films to the other which is close to those of the cast film and solutions. The spectral conversion occurs almost in parallel with that seen in the visible absorption spectra (Figure 2), suggesting that the Raman spectral changes reflect the conversion from the H-aggregate to the monomers. Therefore, the results in Figure 6 indicate that the structure of the -N=N- bond moiety changes slightly upon going from the H-aggregate to the monomer. Since the frequencies of the -N=N- stretching bands in the spectra of the LB films consisting of the monomers are almost identical with those in the spectra of the solutions [15], it is very likely that the

structure of -N=N- bond moiety in the former is close to that in the solutions where the -N=N- bond takes a relaxed conformation. In contrast, the structure of -N=N- bond moiety in the LB films forming the H-aggregate seems to excise conformational distortion
probably due to the aggregation.

Cyclic Temperature Treatments of the LB Film of Azo II

Experiments on the cyclic thermal treatments of a LB film are very important to investigate the effects of the annealing on its orderliness as well as its thermal stability [4,6,8]. As seen in Figure 5, after the cycle to 50 °C the infrared spectrum almost completely returns to the original spectrum. However, the cyclic temperature treatment up to 70 °C causes the irreversible changes not only in the bands due to the chromophoric part but also in those arising from the hydrocarbon chains. Therefore, it seems that the disorder remains in the tails as well as head groups after cycling the temperature to 70 °C. Probably, the orientation and aggregation in the head groups do not recover and the remaining disorder there hinders the reversible conformational changes in the alkyl tails.

Comparison of the Thermal Properties among the LB and Cast Films and Bulk Azo II Dye

The DSC measurement of bulk Azo II dye shows three endothermic peaks at 52.8, 57.1 and 105 °C. The last peak probably corresponds to the melting point while the rest may be due to the onset of disorder. Comparison of this result with those in Figure 4 suggests that the mobility of the hydrocarbon chains increases at slightly lower temperature in the

bulk dye than in the LB film. In contrast, Figure 7 indicates that the cast film has disordered structure at lower temperature than the bulk dye. In our previous paper we showed that the LB and cast films have different kinds of H-aggregates [16]. Therefore, the above mentioned differences in the order-disorder transition may be caused by changes in the molecular aggregation.

Comparison of the Order-disorder Transitions and Thermal Stability between the LB Films of Cadmium Arachidate and Azo II

The order-disorder transitions and thermal stability of LB films consisting of simple molecules such as cadmium arachidate have been explored in some detail by using infrared and Raman spectroscopy [3-8,10-14]. The temperature of the phase transitions and the thermal stability depend upon the head groups, metals of the fatty acid salts, length of hydrocarbon chains, and substrates used [3-8]. To our best knowledge, however, the order-disorder transitions and thermal stability of LB films having a chromophoric group have never been investigated so far. The present study demonstrates that the phase transition and stability of the LB film of Azo II are largely different from those of simple LB films. For example, the LB film of cadmium arachidate shows a two step melting process [4]; in the first step the reversible disordering of the alkyl tails with the ordered head group lattice is observed below a temperature corresponding to the melting point while in the second step irreversible breakup of the head group lattice occurs at the melting point (110 °C). Therefore, the thermal stability is fairly good up to around 100 °C and the order-disorder transition of the alkyl tails is reversible.

In contrast to it, the LB film of Azo II does not show the reversible transition and thermal stability is not good. Probably, the increase in the alkyl chain mobility easily destroys the aggregation and orientation of the bulky head groups and then they make the recovery of their orientation and aggregation difficult.

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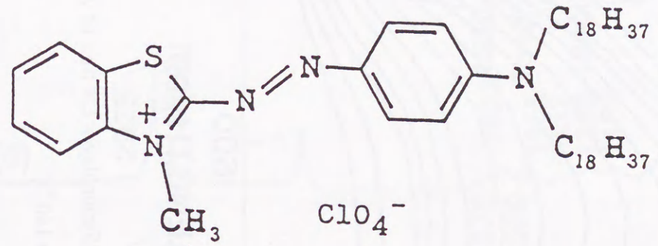

Figure 1. Structure of 2-(4'-(dioctadecylamino)phenylazo)-N-methylbenzothiazolium perchlorate (Azo II).

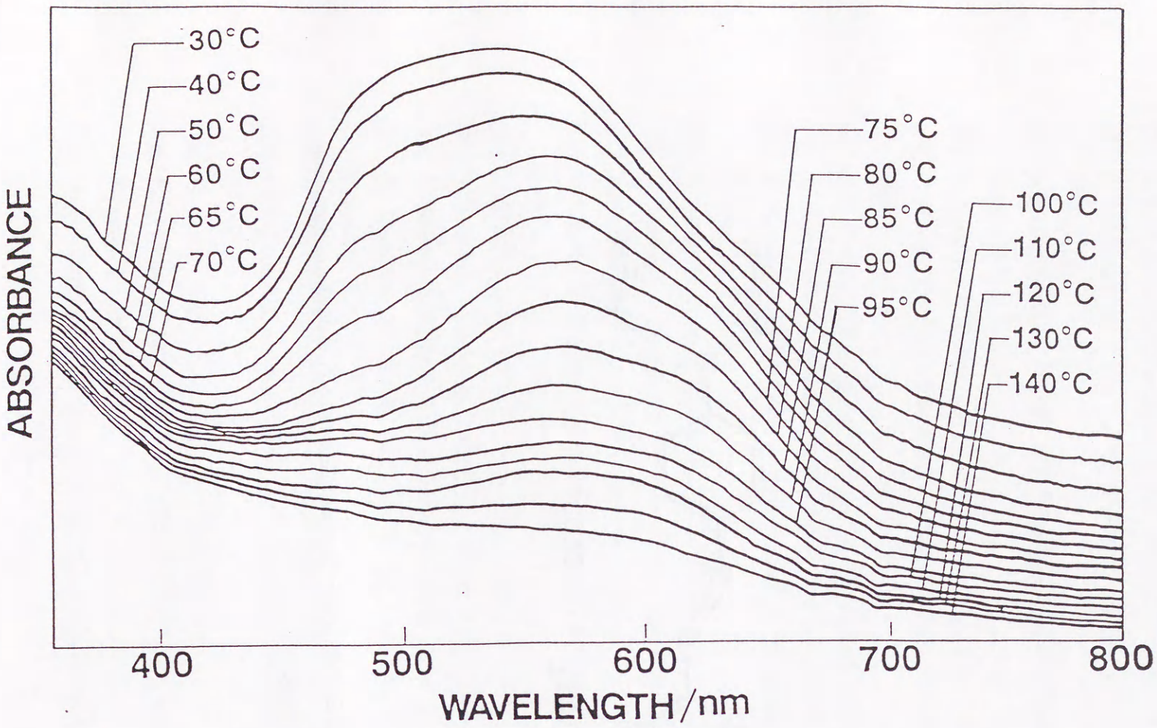

Figure 2. Visible absorption spectra of 15-monolayer LB film of Azo II measured at various temperatures from 30 to 140 °C.

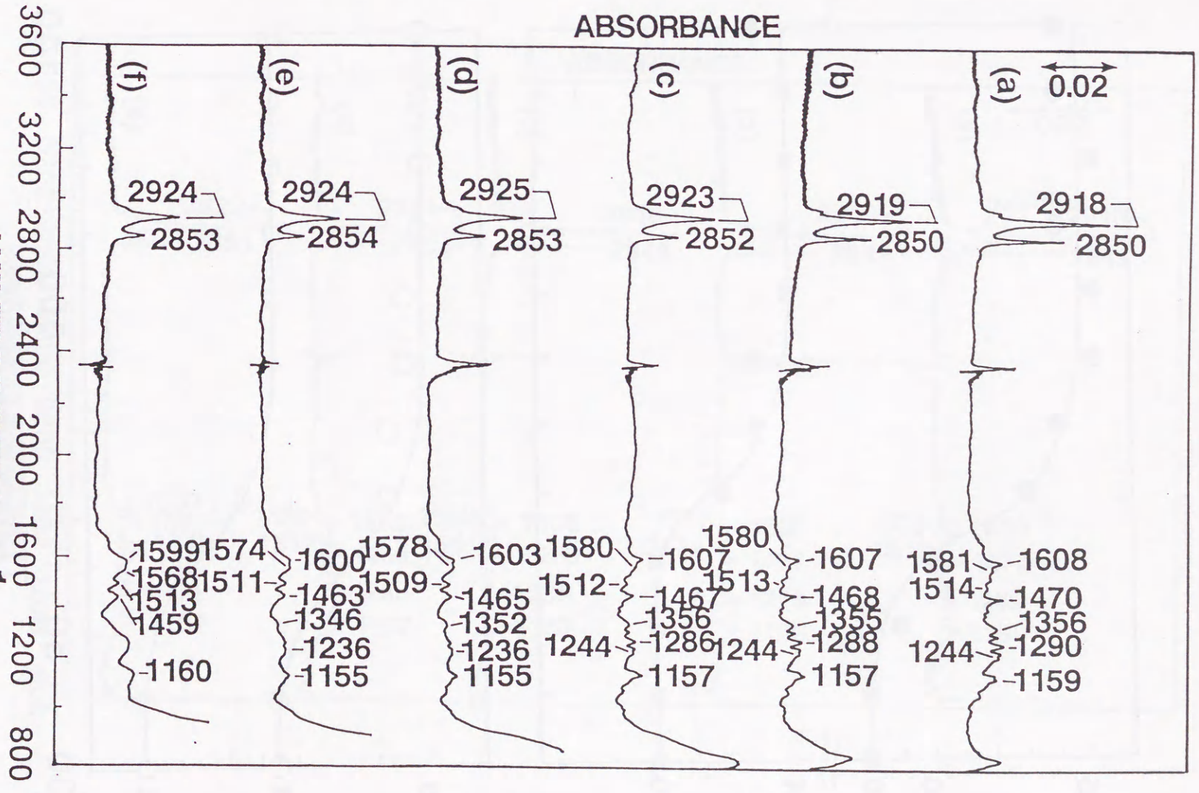

Figure 3. Infrared transmission spectra of 15-monolayer LB film of Azo II measured at 30(a), 50(b), 70(c), 90(d), 110(e), and 140(f) °C. Throughout this paper features appearing near 2350 cm^{-1} are due to carbon dioxide.

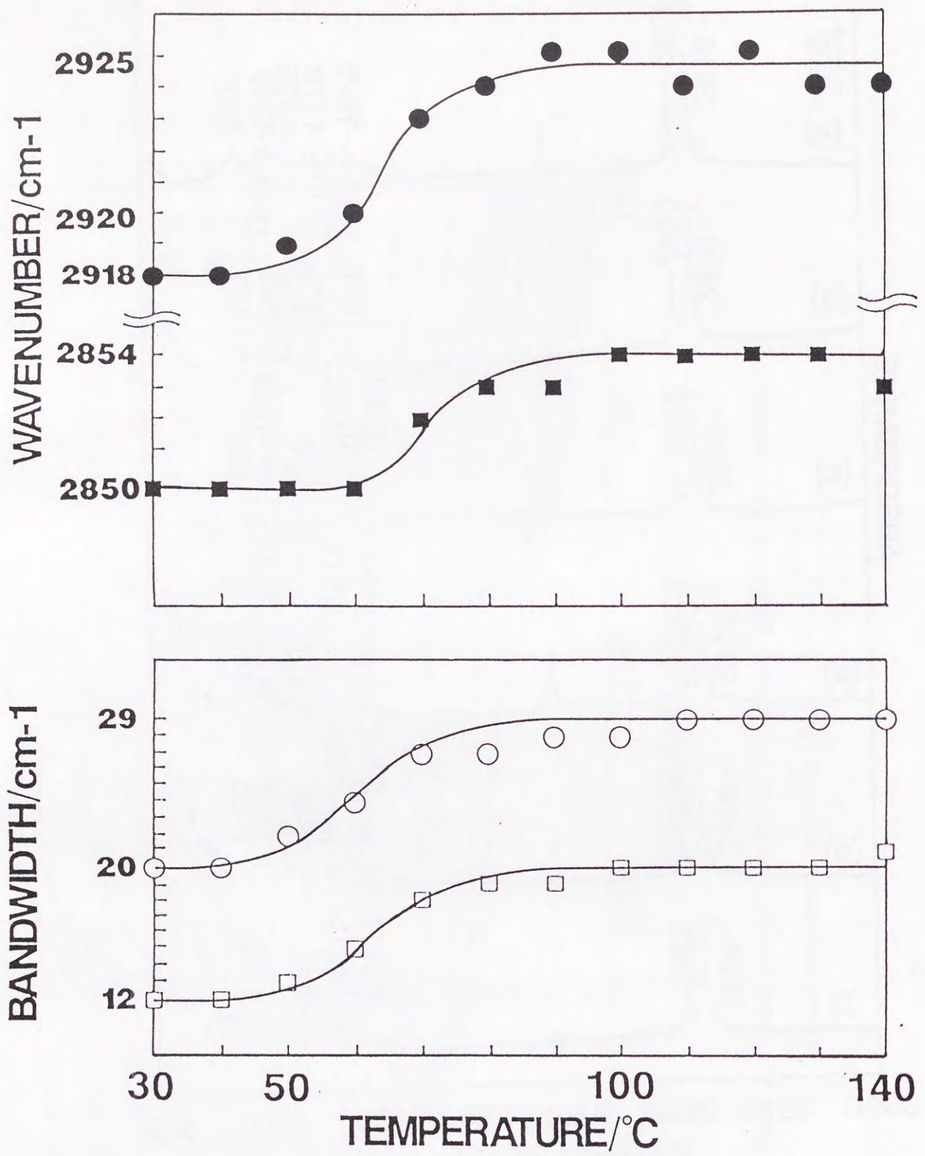

Figure 4. (a) Temperature dependencies of the frequencies of the CH_2 antisymmetric (●) and symmetric (■) stretching bands of the 15-monolayer LB film of Azo II. (b) Temperature dependencies of the bandwidths of the CH_2 antisymmetric (○) and symmetric (□) stretching bands of the 15-monolayer LB film of Azo II.

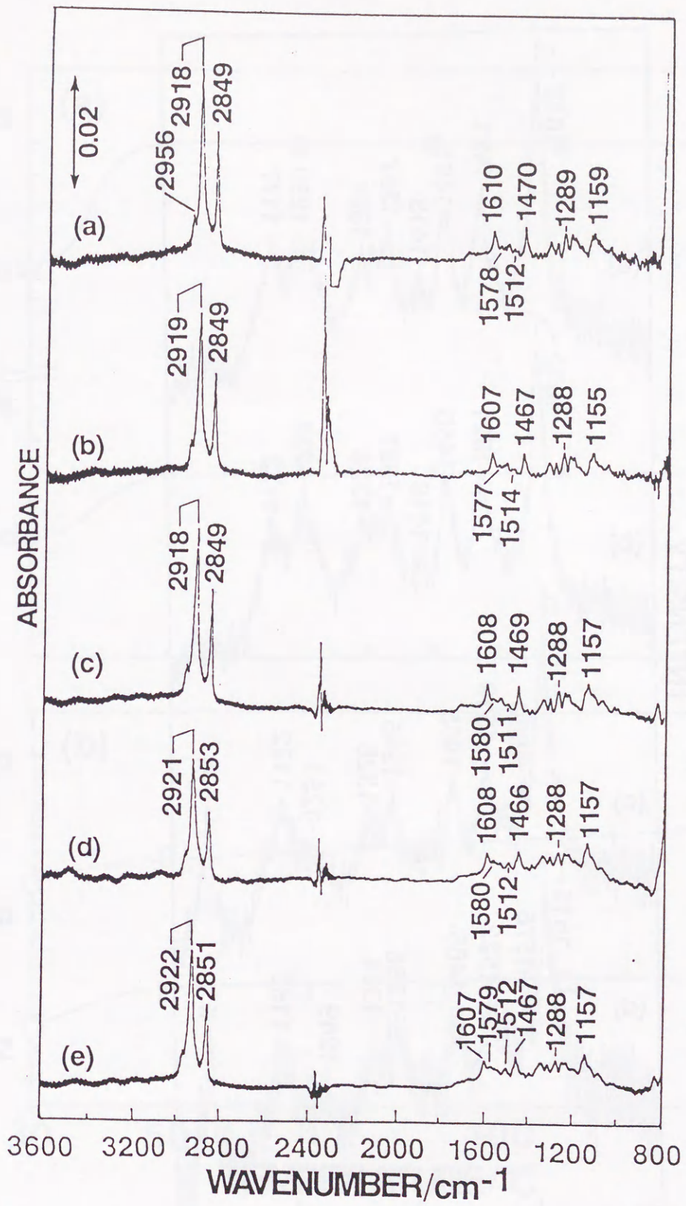

Figure 5. Infrared transmission spectra of 15-monolayer LB film of Azo II obtained before and after cyclic temperature treatments. (a) original spectrum, (b) 50 °C, (c) returned to 30 °C, (d) 70 °C, (d) returned to 30 °C.

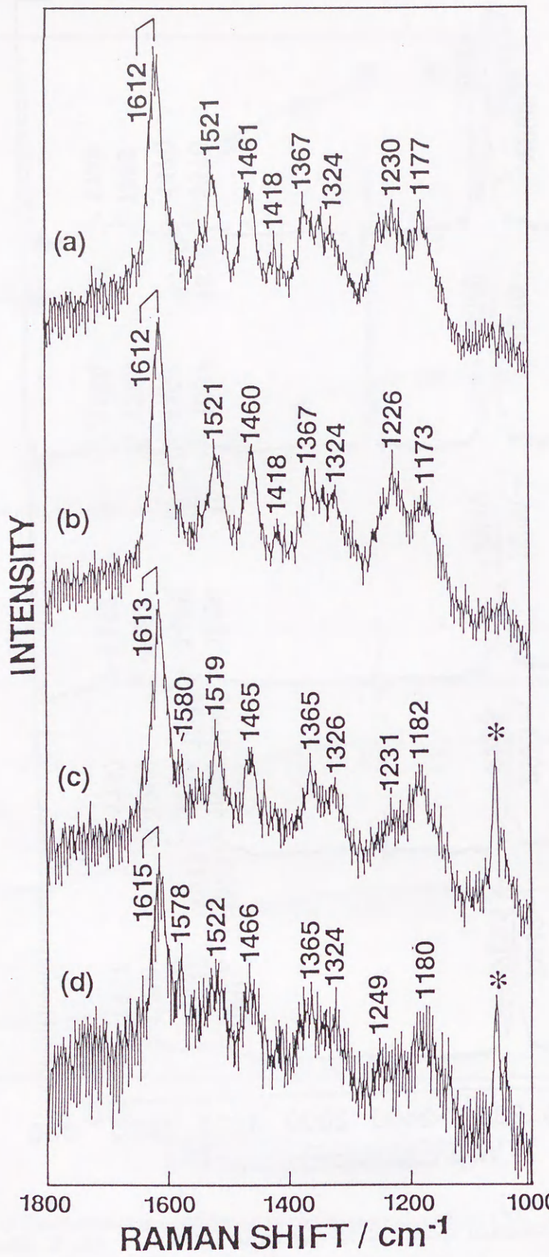

Figure 6. The 488.0-nm excited resonance Raman spectra of 15-monolayer LB film of Azo II measured at 30(a), 50(b), 70(c), and 90 (d)°C.

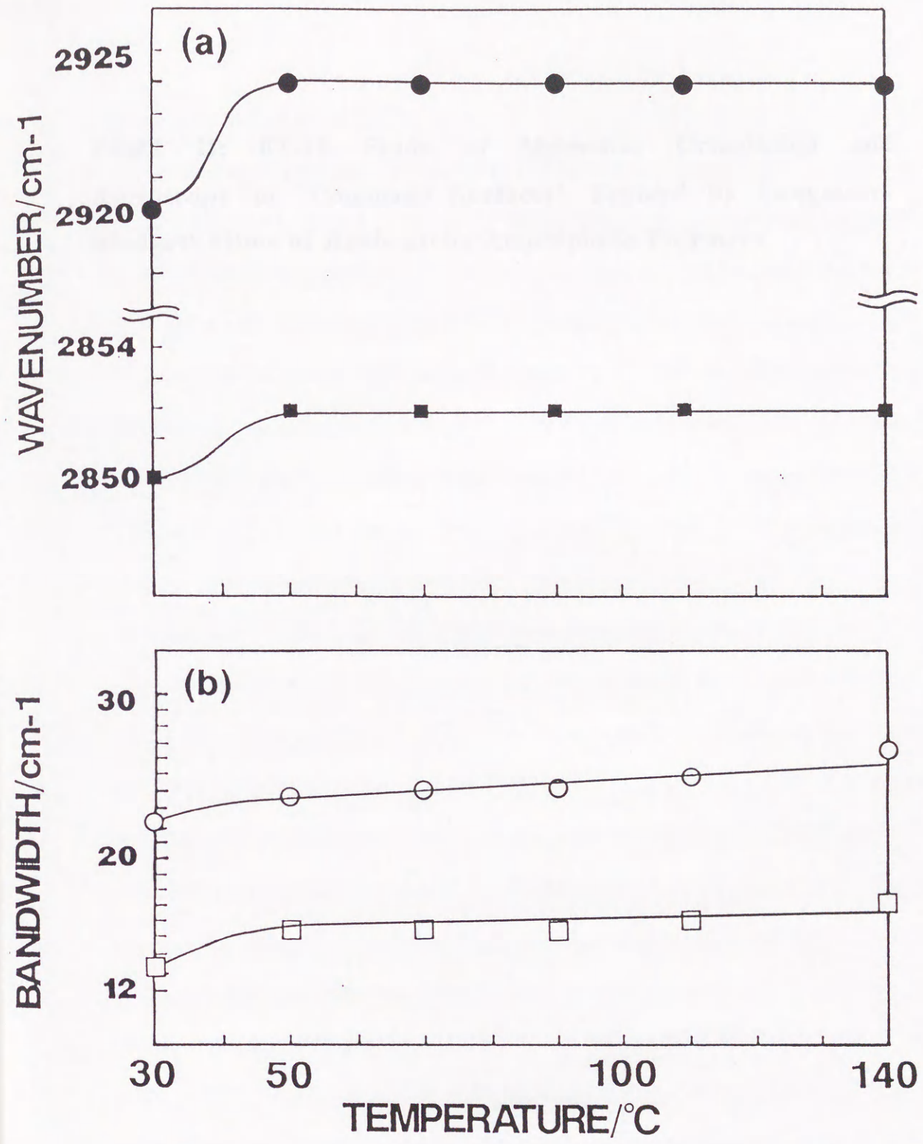

Figure 7. (a) Temperature dependencies of the frequencies of the CH_2 antisymmetric (●) and symmetric (■) stretching bands of the cast film of Azo II. (b) Temperature dependencies of the bandwidths of the CH_2 antisymmetric (○) and symmetric (□) stretching bands of the cast film of Azo II.

PART II: FT-IR Study of Molecular Orientation and Anisotropy in "Command Surfaces" Formed by Langmuir-Blodgett Films of Azobenzene Amphiphilic Polymers

ABSTRACT

FT-IR transmission and reflection-absorption (RA) spectra have been measured for Langmuir-Blodgett (LB) films of *cis*- and *trans*-6Az1-PVA [poly(vinyl alcohol) (PVA) derivative having azobenzene (Az) side chains; Figure 1B] which receive keen interest as a highly photoreactive layer for the surface photoregulation of nematic liquid crystal (LC) alignment. Vibrational frequencies of CH_2 antisymmetric and symmetric stretching bands show that the hydrocarbon chain in the multi-monolayer films contains *gauche* conformers. Probably, the disorder of the hydrocarbon chain increases its mobility, making the contact between the LC molecule and 6Az1-PVA feasible. Comparison of band intensities between the IR transmission and RA spectra indicates that the hydrocarbon chain and -O-CH_2-CO-O- linkage assume rather randomly oriented states. This conclusion is in good agreement with the suggestion by Seki *et al.* that the Az side chains do not have highly ordered structure prior to the deposition of LC molecules, and that the normal orientation of Az side chains with respect to the substrate plane is caused by an induced fitting between the two-dimensional Az host layer and guest LC molecules. Polarized FT-IR spectra have been obtained for LC molecules photoregulated by the LB films of *cis*- and *trans*-6Az1-PVA. The spectra show that the LC molecules on the LB film of *cis*-6Az1-PVA are laid on the surface of the substrate with its long axis perpendicular to the polarized UV light irradiated. The LC molecules on the LB film of *trans*-6Az1-PVA form homeotropic orientation with respect to the substrate surface. The efficiency of the polarization on the anisotropy of the LB film of *cis*-6Az1-PVA has been studied by irradiating polarized UV lines with their polarization planes perpendicular and parallel to the dipping direction in turn. It has been found that the alternation of dichroism occurs without the irradiation of blue line, and that the polarized lines have different efficiency. The polarized IR spectra also suggest that the anisotropy induced by light illumination is superior to that imposed during the dipping process.

INTRODUCTION

Alignment behaviors of liquid crystals (LC) by the surface molecular layer structure have long been a matter of active investigations [1-4]. It has recently been demonstrated that reversible homeotropic-planar photochemical alignment controls of nematic LC can be performed by the *cis-trans* photochromic reaction of azobenzene (Az) layers attached on the cell substrates [5-14]. It was proposed to term these photofunctional surfaces "command surfaces" because this phenomenon involves alignment changes of *ca.* 10^4 LC molecules commanded only by a couple of Az units on the surface (see Figure 1 A). Such Az surface layers can be prepared by applying various kinds of methods such as covalent bond formation of silylation [5,8,10], or Michael addition [11,12], simple spin coating of Az polymers [6,9], and Langmuir-Blodgett (LB) film method [7,13,14].

Seki *et al.* [7,13,14] have been focusing their research activities on the LB technique. This approach offers molecularly tailored Az layers, and may be most useful to understand the command surface phenomenon at the molecular level. Besides its utility in molecular tailoring, the LB technique holds a superior feature that in-plane structural anisotropy may be imprinted during the dipping process. From the requirement of highly photoreactive Az LB layers, poly(vinyl alcohol) (PVA) derivatives having Az side chains (6Az*n*-PVA, 6 and *n* denoting the carbon length of the tail attached to the Az part and spacer length connecting the Az unit and the PVA backbone, respectively; Figure

1B) have been employed. In the LB films of 6Az*n*-PVA, the PVA backbone sterically prevents tight aggregation of the Az side unit, and consequently the Az unit undergoes readily *cis-trans* photoisomerization [15,16]. By using these molecular films, much knowledge has been accumulated regarding (i) effects of the side chain structure, the Az packing density, and the number of transferred layers, (ii) in-plane anisotropic properties with respect to the dipping process, and (iii) reorienting behaviors with polarized UV light illumination, and so forth [13,14].

In order to understand the mechanism of photoregulations and reorientation behaviors of LC molecules upon the UV light irradiation, structural characterization of the LB films should be of particular importance. Thus far, molecular orientation and structural justification of the LB films of 6Az*n*-PVA have been investigated only by UV-visible absorption spectroscopy. The purpose of the present study is to explore more details of the structural characteristics of the LB films of 6Az*n*-PVA and the LC orientation by using FT-IR spectroscopy. This technique, which is a powerful non-destructive structural probe for various kinds of molecular assemblies, provides information about molecular orientation in a LB film, molecular conformations of hydrocarbon chain and chromophoric part, subcell packing of the chain, anisotropy of the film, and so on [17-22]. In this study, 6Az1-PVA (methylene spacer length of 1) is chosen as the LB film for which conformation of the hexyl tail can be investigated easily.

EXPERIMENTAL

Sample Preparation

The synthesis of 6Az1-PVA was reported by Seki *et al*. [6,14] DON-103 was a generous gift from Dr. H. Takatsu (Dai Nippon Ink and Chemicals, Inc.). The LB films of 6Az1-PVA were prepared by using a Kyowa Kaimen Kagaku Model HBM-AP Langmuir trough with a Wilhelmy balance. The 6Az1-PVA dissolved in chloroform (1 mM) was irradiated by UV-lamp (365 nm) for *ca.* 15 min to isomerize the *trans* form into the *cis* form. The solution so-obtained was spread onto an aqueous subphase of doubly distilled water (295 K). After evaporation of the solvent, the monolayer was compressed at a constant rate of 30.0 cm^2min^{-1} upto the surface pressure of 20 mNm^{-1}. The π-A isotherm was almost identical with that obtained previously [16].

The monolayers were transferred by the vertical dipping method onto CaF_2 plates (for IR transmission and UV-visible absorption measurements) or Au-evaporated glass slides (for IR reflection-absorption (RA) measurements) at a given pressure. The transfer ratio was found to be at least 0.90 throughout the experiments. The LB films treated in this paper have the Y-type structure. All the procedures of LB film fabrication were performed under dimmed red light.

The LC was sandwiched between LB film-modified and clean CaF_2 substrates. The estimated cell gap was 10 μm. A 355-nm line from a THG of Nd;YAG laser (Spectra Physics 3800S) and a 457.9-nm line

from an Ar laser (Spectra Physics 2016-05) were employed for the photo-isomerization to *cis* and *trans* forms of the azobenzene group, respectively. The laser lines were expanded to 20-30 mm of diameter and the laser power of the UV and visible lines were 300 and 100 mW, respectively. For the photo-isomerization of the LC cell the lines were introduced from the LB film side to avoid a change in the polarization of the laser light. The photo-isomerization occurred alternatively and no photo-decomposition was induced by the laser irradiation. Hereafter, the light with the polarization planes parallel and perpendicular to the dipping direction is named 0°- and 90°-polarized light, respectively. Figure 2 displays the correlation between the dipping direction and the polarization planes of inducing (UV / Visible) and probing (IR) light.

Measurements of Spectra

FT-IR spectra were measured with a JEOL JIR-6500 FT-IR spectrometer equipped with an MCT detector. All the data were collected at a spectral resolution of 4 cm^{-1}, and typically, 300 and 50 interferograms were coadded for the measurements of the IR spectra of the LB films and LC cells, respectively. For the polarized IR measurements a JEOL IR-OPT02 polarizer was placed. The IR RA spectra were obtained by using a JEOL IR-RSC 110 reflection attachment at the incident angle of 80°, together with the above polarizer.

UV-visible absorption spectra were recorded on a Shimadzu UV-

3101PC spectrophotometer. For the polarized measurements a dichroic sheet polarizer (MELLES GRIOT) was placed in front of the LB films.

RESULTS AND DISCUSSION

Structure of the LB Films of 6Az1-PVA

Figure 3 shows FT-IR transmission spectra of 1-(a), 3-(b), and 9-(c) monolayer LB films of 6Az1-PVA. Intense bands near 2920 and 2850 cm^{-1} are assigned to CH_2 antisymmetric and symmetric stretching modes of the hydrocarbon chain of the chromophore, respectively. The frequencies of the CH_2 stretching bands are very sensitive to the conformation of the hydrocarbon chain [23,24]; the low frequencies (2920 and 2850 cm^{-1}) of the bands are characteristic of the highly ordered (*trans*-zigzag) alkyl tail while their upward shifts are indicative of the increase in conformational disorder, *i.e. gauche* conformers in the hydrocarbon chain. The CH_2 stretching bands appear at 2920 and 2850 cm^{-1} in the spectrum of single monolayer film, but they show an upward shift with increasing the number of monolayer. It seems therefore that the hydrocarbon chain of 6Az1-PVA is ordered, *i.e.*, *trans*-zigzag in the single monolayer film while that in the multi-monolayer films contains *gauche* conformers.

A band at 1756 cm^{-1} is due to a C=O stretching mode, and those at 1600 and 1498 cm^{-1} are assigned to ν_{8a} and ν_{19a} modes of the benzene rings, respectively [25]. It is noted that the C=O stretching band has a shoulder near 1732 cm^{-1}. This observation suggests that some of the C=O groups form a hydrogen bonding, probably, with the hydroxy group of PVA. A broad band at 1201 cm^{-1} seems to arise from two C-O-C antisymmetric stretching modes while a sharp feature at 1153 cm^{-1} may

be due to a =N-Ph stretching mode [25]. A CH out-of-plane deformation mode of the benzene rings appears near 840 cm^{-1} [25]. Frequencies of these bands are very close to those for a solid state (KBr disc), indicating that the structure of chromophoric part of the molecule changes little between the LB film and solid state.

Figure 4 compares UV-visible absorption spectra of 9-monolayer LB films of 6Az1-PVA in *cis* (a) and *trans* (b) configurations. Figure 4(a) and (b) are almost identical with those previously reported by Seki *et al.* [14]; the UV-visible absorption spectra of the *cis* and *trans* forms are characterized by weak bands near 312 and 442 nm and an intense band at 347 nm, respectively.

In Figure 5 IR RA spectra of 9-monolayer LB films of 6Az1-PVA in *cis* (a) and *trans* (b) configuration are compared. In contrast to the UV-visible spectra, the IR RA spectra of the LB films of 6Az1-PVA in *cis* and *trans* forms are very similar to each other except that the relative intensities of bands at 1601, 1587, 1155, and 843 cm^{-1} are slightly stronger in the spectrum of the *trans* configuration. Comparison of band intensities in the IR transmission and RA spectra of LB films enables us to discuss the molecular orientations of the hydrocarbon chain and chromophore of 6Az1-PVA; according to the surface selection rule in IR RA spectroscopy [26-28], vibrational modes with their transition moments perpendicular to the substrate surface are enhanced in a RA spectrum. Comparison of band intensities between the spectra of LB films and solid states also provides useful information

about the molecular orientation in the LB films. From those comparisons (the IR transmission spectrum of the 9-monolayer LB film of *trans* 6Az1-PVA is shown in Figure 3(c)), it may be concluded that the hydrocarbon chain, -O-CH_2-CO-O- linkage, and C=O group take randomly oriented states in the LB films of *cis*- and *trans*-6Az1-PVA because the relative intensities of the bands due to the CH_2 antisymmetric and symmetric stretching, C=O stretching, and C-O-C antisymmetric stretching modes do not change significantly between the IR transmission and RA spectra of the 9-monolayer LB films of *cis*- and *trans*-6Az1-PVA and between the IR transmission spectra of the LB films and solid states. It seems likely that 6Az1 side chain takes a randomly oriented state except for the -Ph-N=N-Ph- moiety because the two-dimensional packing density of the Az unit is low.

Now, we can discuss relation between the molecular orientation in the LB films of 6Az1-PVA and their ability as command surfaces. Quite recently, Seki *et al.* [14] suggested from UV-visible spectral changes of the LB films of 6Az*n*-PVA that normal orientation of Az side chains with respect to the substrate plane is induced from a rather randomly oriented state upon contact with the LC molecules. They recognized this phenomenon as an induced fitting phenomenon between the two-dimensional Az host layer and guest LC molecules. The present conclusions for the molecular orientation are in good agreement with their conclusion that the Az side chains do not have highly ordered structure prior to the deposition of LC molecules. It was also reported

that the photoregulation of LC does not work in the single monolayer film but it is very effective in the 9-monolayer film [14]. It is probable that the hydrocarbon chain has larger mobility in the 9-monolayer film because it has increased conformational disorder, *i.e.*, *gauche* conformers, and therefore the contact between the LC molecules and 6Az1-PVA becomes feasible.

Polarized FT-IR spectra of the 9-monolayer LB film of *cis*-6Az1-PVA were measured. Perpendicular (a) and parallel (b) lights with respect to the dipping direction of the film were used to observe the spectra. The two spectra are almost identical to each other, again indicating that the 6Az1 groups do not have highly ordered orientation.

Anisotropy in the LB Films of 6Az1-PVA Observed by LC Alignment

Figure 6 shows polarized FT-IR transmission spectra of DON-103 photoregulated by the 9-monolayer LB film of *cis*-6Az1-PVA. The 0°-polarized UV and visible lines (*i.e.* parallel to the dipping direction; Figure 2) were employed for the photo-isomerizations. All the observed bands are assignable to DON-103; the bands from the thin LB films are too weak to be observed. Bands at 2927 and 2856 cm^{-1} are due to CH_2 antisymmetric and symmetric stretching modes of both the hydrocarbon chain and cyclohexane ring of DON-103, respectively, and those at 1751 and 1450 cm^{-1} are assignable to its C=O stretching and CH_2 scissoring modes, respectively. The transition moments of those modes are nearly perpendicular to the long axis of the LC molecule.

Bands at 1595 and 1506 cm^{-1} may be assigned to ν_{8a} and ν_{19a} modes of the benzene ring, respectively, because it is well known that para-disubstituted benzenes give a weak to medium IR band due to ν_{8a} near 1600 cm^{-1} and a fairly intense band due to ν_{19a} near 1500 cm^{-1} [25]. Bands at 1206 (shoulder) and 1194 cm^{-1} arise from C-O-C asymmetric stretching modes of Ph-O-R' and C-O-Ph, respectively [25]. Those four bands have their transition moments parallel to the long axis. The spectra of the LC on the LB film of *trans*-6Az1-PVA change little with the angle of probe light while those of *cis*-6Az1-PVA obviously show dichroism; the bands arising from the modes with their transition moments parallel to the long axis increase with the increase in the angle whereas those with their transition moments perpendicular to the axis decrease. The observation for the LC on the LB film of *cis*-6Az1-PVA indicates that the LC molecules are laid on the surface of the substrate and the direction of its long axis is perpendicular to the polarized UV light irradiated for the photoregulation. This conclusion is consistent with that reached previously from a visible absorption study using a dichroic dye as a dopant of the LC phase [14]. The polarized FT-IR spectra of the LC on the LB film of *trans*-6Az1-PVA were also obtained with the polarized visible lines, but they did not show dichroism, implying that the LC molecules form homeotropic orientation with respect to the substrate surface.

Polarized FT-IR spectra of the LC on the LB film of *cis*-6Az1-PVA irradiated by 90°-polarized (*i.e.* perpendicular to the dipping

direction; Figure 2) light are shown in Figure 7. In contrast to the dichroism observed for the 0°-polarized irradiation (Figure 6), the bands due to the modes with their transition moments parallel to the long axis become weak with the increase in the angle whereas those with their transition moments perpendicular to the axis become strong. It seems therefore that the anisotropy of the LB film of 6Az1-PVA in the *cis* form reflects the polarization of UV line irradiated.

It has recently been observed that LC molecules are reoriented by illumination of linearly polarized UV light; LC molecules reorient orthogonal to the polarization plane [14]. Since LB films possess the in-plane structural anisotropy imposed by the dipping process, it is of particular interest to compare the orienting factors between the LB film structure and the polarized UV light. They deduced the following conclusions from their experiments of 1-, 3-, 5-, 7-, and 9-monolayer LB films of 6Az1-PVA, 6Az5-PVA, and 6Az10-PVA: (i) a certain length of methylene spacer between the backbone and Az unit (n=5, 10) is needed for the reorientation of LC and (ii) it occurs at the minimum number of deposition of photoresponsive cells (three-layered 6Az5-PVA and one-layered 6Az10-PVA, see Table II of ref. 14); accumulated deposition imposes strong in-plane anisotropy in the LB film structure with regard to the dipping direction and thus suppresses the reorienting effect. As for 9-monolayer 6Az1-PVA LB film, LC molecules were oriented parallel to the dipping direction in the experiments [14] while in the present experiments they are reoriented by the polarized UV light,

the direction being orthogonal to the polarization plane. The discrepancy between the last and present cases might be caused by the difference in the light intensity employed; they used UV (366 nm) light selected using Corning glass filters 7-51 from lights of a super high-pressure mercury lamp while we employed a 355-nm line (300 mW) from a THG of Nd;YAG laser.

The efficiency of the polarization on the anisotropy of the LB film of *cis*-6Az1-PVA is compared in Figure 8A and B. Figure 8A shows the polarized FT-IR spectra of DON-103 photoregulated by the film for which 90°-polarized UV line was irradiated for 1 minute after enough (10 minutes) irradiation of 0°-polarized UV line. On the other hands the spectra of the LC on the film irradiated by 0°-polarized UV line (1 minute) after the irradiation of 90°-polarized UV line (10 minutes) are shown in Figure 8B. Interestingly, the alternation of dichroism occurs without the irradiation of blue line, and its efficiency is different between the 0°- and 90°-polarized lines due to the dipping-induced structural anisotropy of the LB film.

It has become clear from the study by Seki *et al.* [14] that the LB films of 6Az*n*-PVA have in-plane anisotropy imposed by the dipping process. However, the present results for the polarized FT-IR spectra of both the LB film itself and LC molecules photoregulated by the film suggest that the in-plane anisotropy is fairly weak even in the 9-monolayer films and not superior to that induced by light illumination. Therefore, it seems that the anisotropy of the LC layer is induced by the

macroscopic morphology of the LB film as 'Command Surfaces'.

CONCLUSION

Conclusions obtained in the present study can be divided into two. One is concerned with the structure of the LB films of 6Az1-PVA and another is related to their anisotropy. As for the structure, the following conclusion can be reached: the hydrocarbon chain and -O-CH_2-CO-O- linkage of 6Az1-PVA take rather randomly oriented states in the LB films and the chain in the multi-monolayer films contains *gauche* conformers. These rather randomly oriented structure may be preferable for the induced fitting between the two-dimensional Az host layer and guest LC molecules.

The present study also provides the following conclusions for the anisotropy of the LB films: (i) the LC molecules photoregulated by the LB film of *cis*-6Az1-PVA are laid on the substrate surface with its long axis perpendicular to the polarized UV light irradiated while those on the film of *trans*-6Az1-PVA form homeotropic orientation with respect to the substrate surface; (ii) 0°- and 90°-polarized UV lines have different efficiency on the anisotropy of the LB film of *cis*-6Az1-PVA, and the alternation of dichroism takes place without irradiating blue line; (iii) the anisotropy induced by the laser illumination is superior to that imposed during the dipping process.

Finally, it has been also demonstrated here that FT-IR spectroscopy is a very powerful tool not only for investigating the structure of the LB films but also for exploring alignment of LC molecules and anisotropy of the films.

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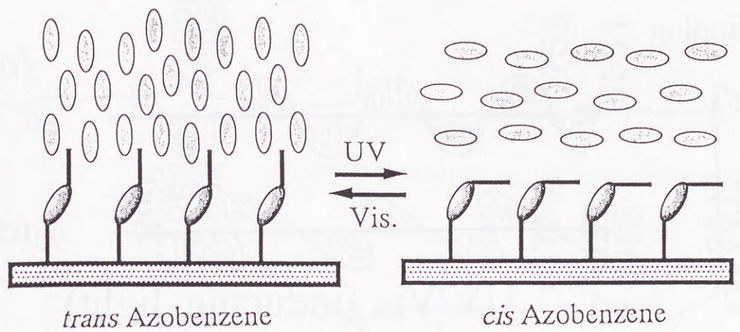
(A)



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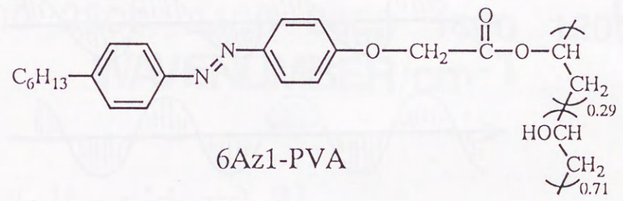
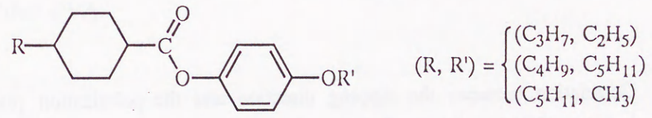


6Az1-PVA



DON-103

Figure 1. A; Schematic illustration of 'Command Surface'.
B; Molecular structure of 6Az1-PVA (a) and DON-103 (b).

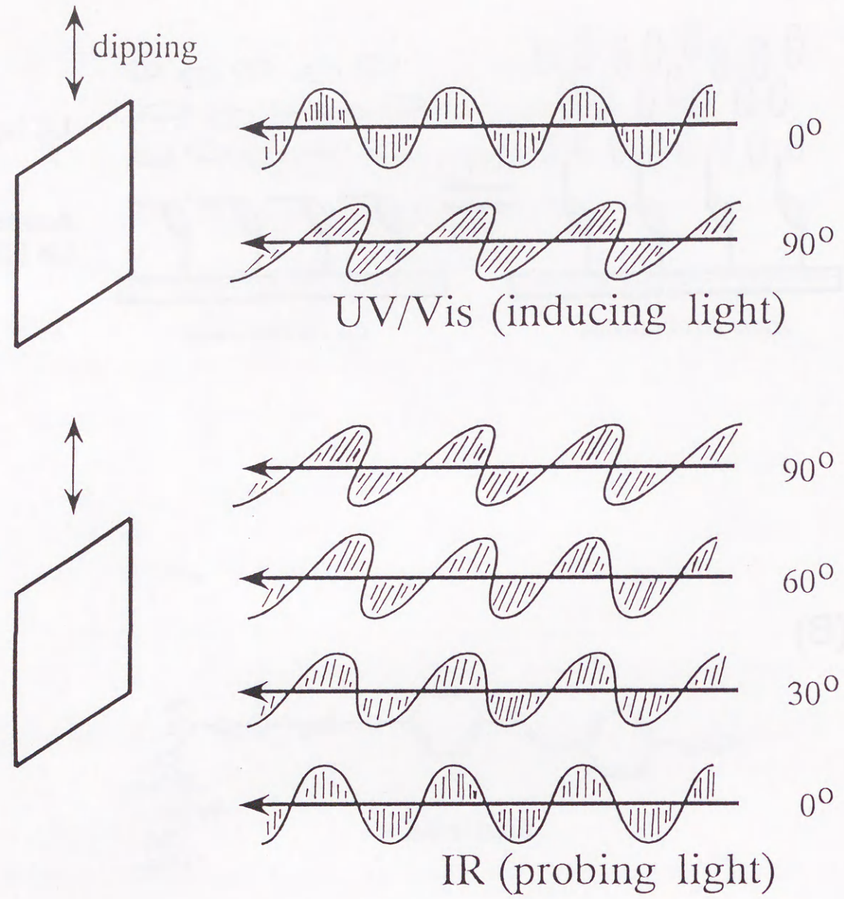


Figure 2. Correlation between the dipping direction and the polarization planes of inducing (UV / Visible) and probing (IR) light.

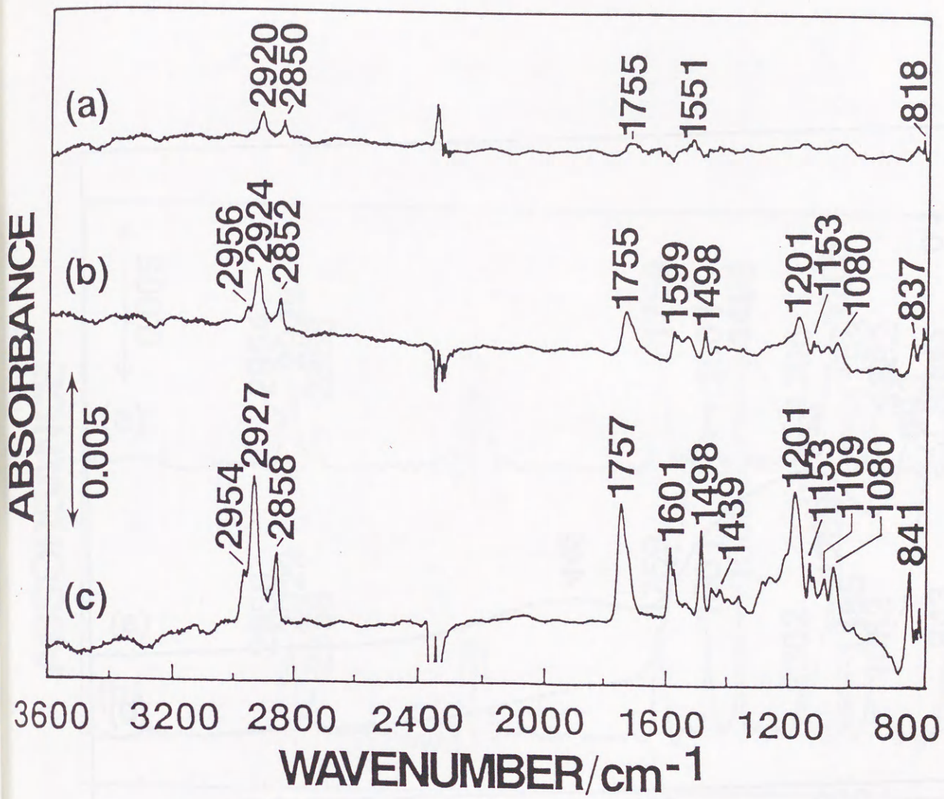


Figure 3. FT-IR transmission spectra of 1-(a), 3-(b), and 9-(c) monolayer LB films of 6Az1-PVA.

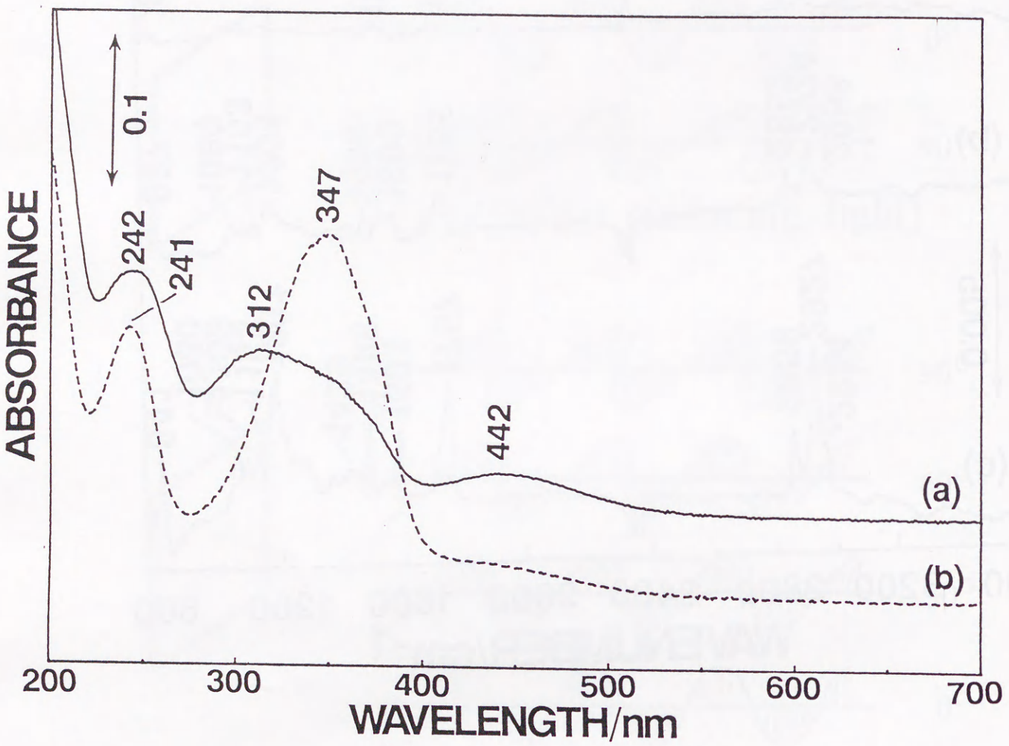


Figure 4. UV-visible absorption spectra of 9-monolayer LB films of *cis*-(a) and *trans*-(b) 6Az1-PVA.

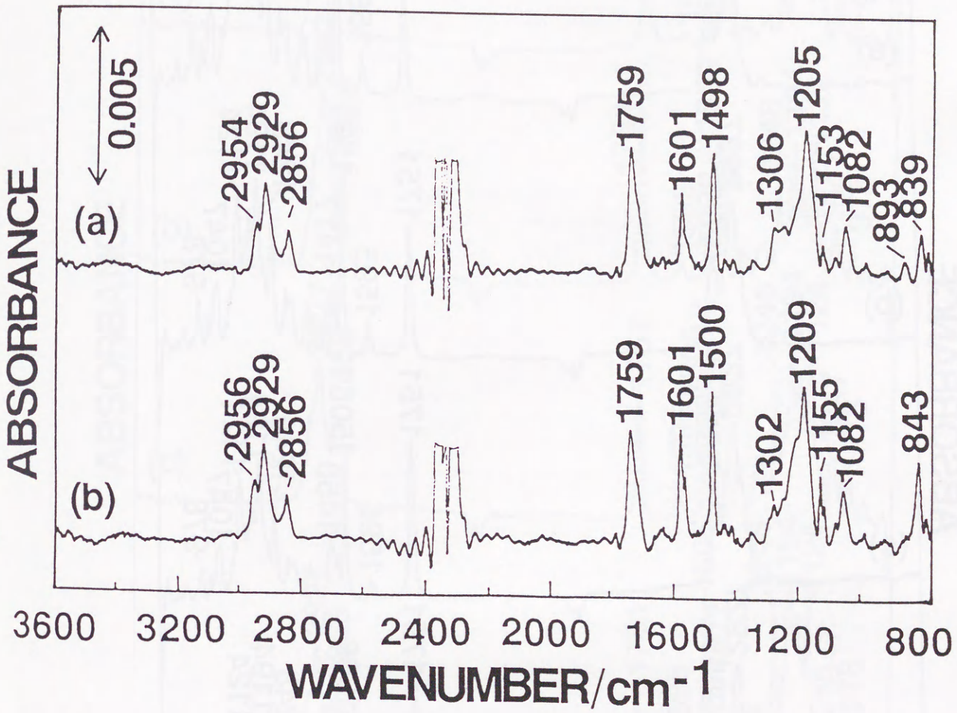


Figure 5. FT-IR RA spectra of 9-monolayer LB films of *cis*-(a) and *trans*-(b) 6Az1-PVA.

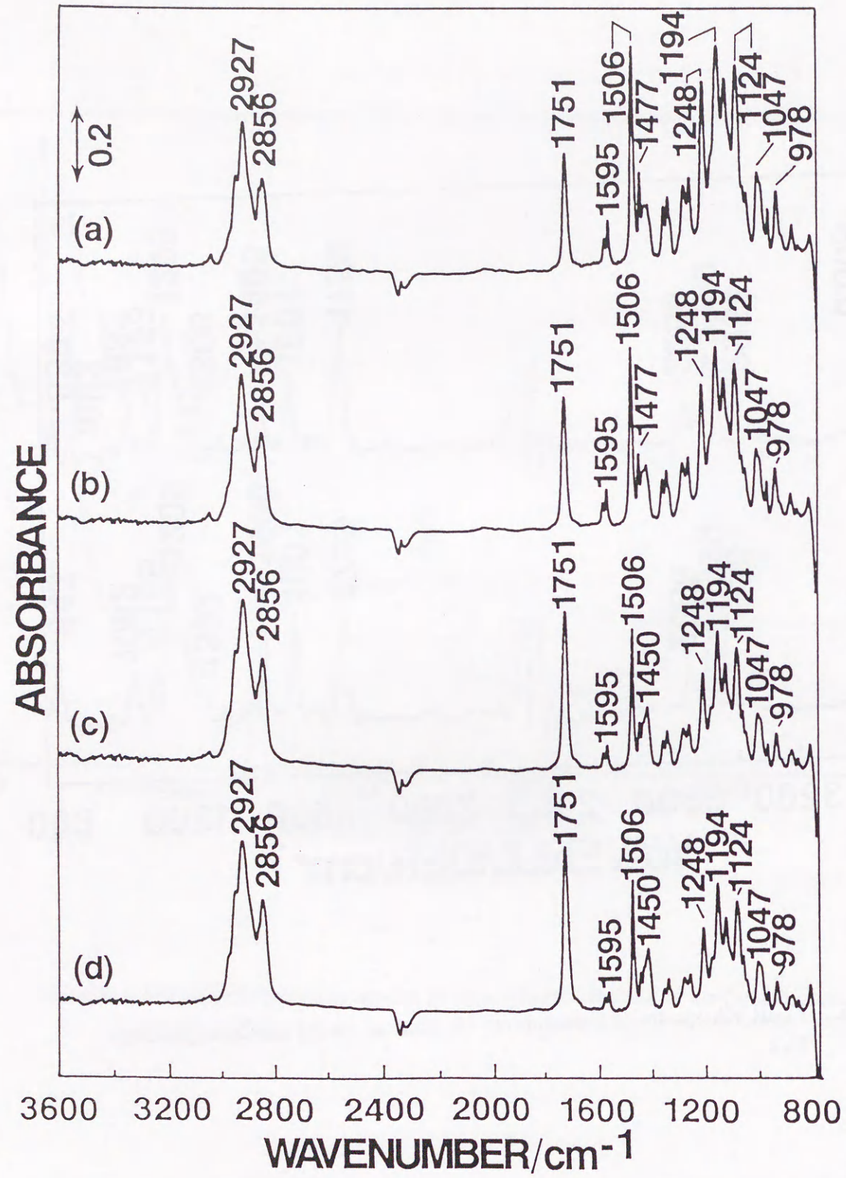


Figure 6. Polarized FT-IR transmission spectra of DON-103 photoregulated by the LB film of *cis*-6Az1-PVA. A 0°-polarized UV (355 nm) line was used for the isomerization. The angles of probe lights are 90°(a), 60°(b), 30°(c), and 0°(d) from the dipping direction, respectively.

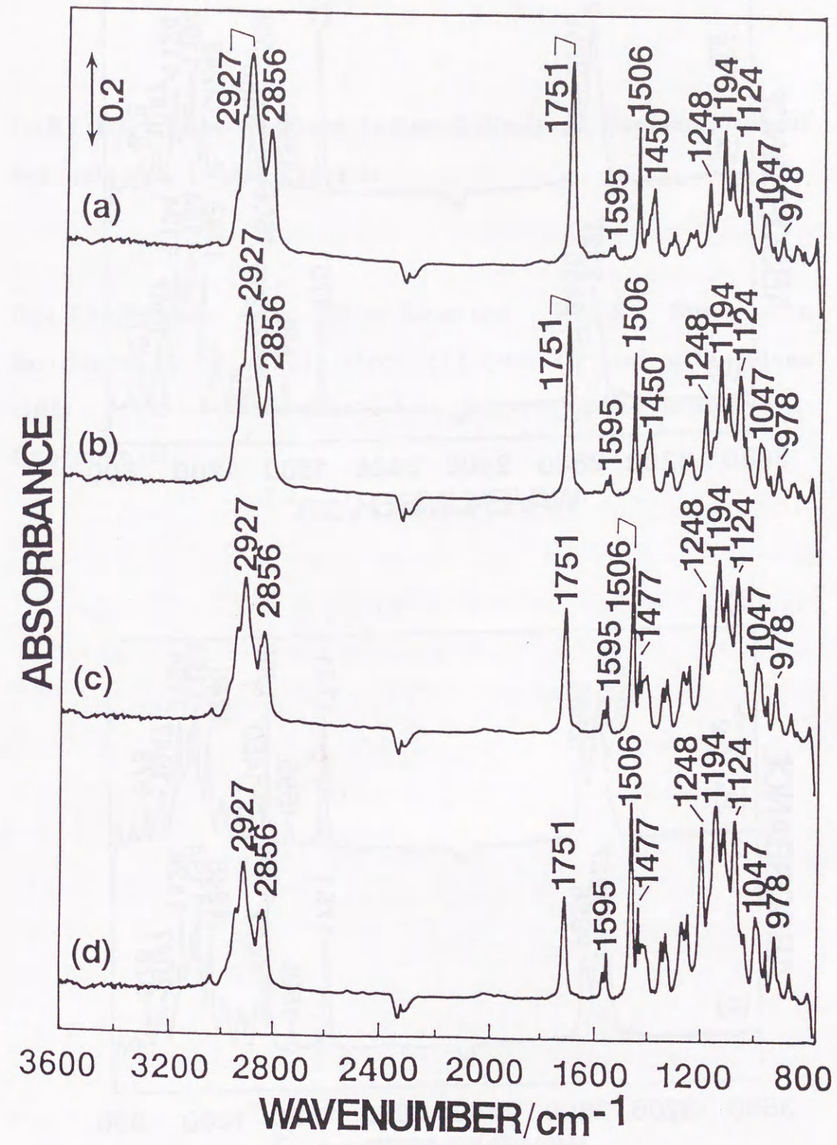


Figure 7. Polarized FT-IR transmission spectra of DON-103 photoregulated by the LB film of *cis*-6Az1-PVA. A 90°-polarized UV line was used for the isomerization. The angles of probe lights are the same as those in Figure 6.

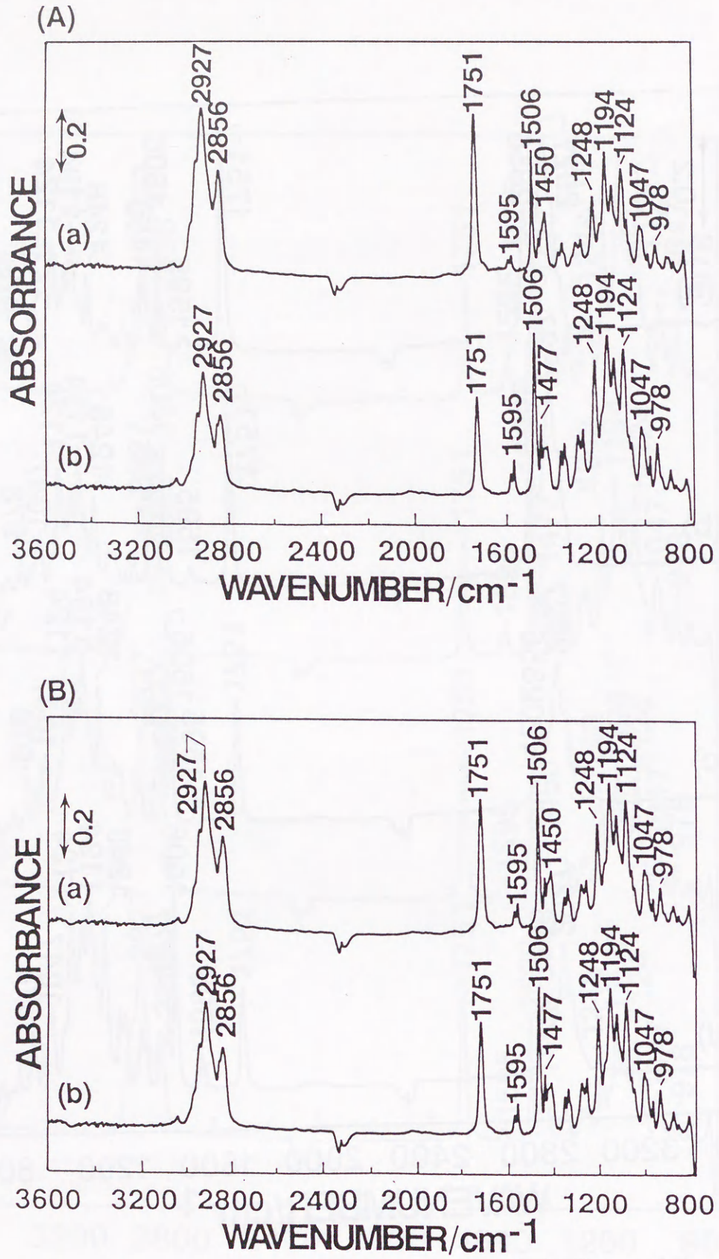


Figure 8. Polarized FT-IR transmission spectra of DON-103 photoregulated by the LB film of *cis*-6Az1-PVA. (A) A 90°-polarized UV line was irradiated after 0°-polarized UV line. (B) A 0°-polarized UV line was irradiated after 90°-polarized UV line. Perpendicular (a) and parallel (b) lights with respect to the dipping direction were employed to observe the spectra.

PART III: Time-Resolved Infrared Study on Reorientation of Ferroelectric Liquid Crystals

SECTION III-1: A Time-Resolved FT-IR Study on Reorientation of a Ferroelectric Liquid Crystal with tolane ring, (S)-4-Methylhexyl-4-[4-(decyloxy)phenylethynyl]-2-fluorobenzate

ABSTRACT

Transient infrared spectra of ferroelectric liquid crystals with tolane ring, (S)-4-Methylhexyl-4-[4-(decyloxy)phenylethynyl]-2-fluorobenzate, under different conditions in the smectic C* phase have been measured by use of an asynchronous time-resolved FT-IR method. The band assignments were made on the basis of the polarized FT-IR spectra and FT-Raman spectrum. The time-resolved study indicates that the reorientation occurs immediately after the electric field is applied. The molecule reorients as a unit instead of the expectation that the rigid core of the molecule is more sensitive to the electric field than the hydrocarbon chains. The spectra obtained under the different conditions suggest that the temperature and applied voltage alter the tilt angle and angular velocity of reorientation of the liquid crystal, respectively. Of particular note is the behavior of the carbonyl band; this band, usually strong in infrared spectra, is very weak in the time-resolved spectra.

INTRODUCTION

Liquid crystals (LCs) are widely used for various kinds of devices, especially in display systems in which their ability to reorientate in the electric field is utilized [1,2]. In spite of this capability, the detailed mechanism of electric-field-induced reorientation is still not fully understood. Especially, the efficiency of the conditions surrounding the LC molecule must be investigated in molecular segment level to understand the mechanism of orientation. Recently, there has been great progress in the field owing to new possibilities offered by time-resolved infrared spectroscopy [3-5]. This method enables us to obtain information about the motion of the whole molecule as well as details of the time course of the reorientation of particular fragments of the molecule. However, most time-resolved infrared studies have so far dealt with nematic LC [3-6]; there have been very few reports concerning ferroelectric liquid crystals (FLCs) [7].

In this section, the results of a polarized time-resolved FT-IR (TRFTIR) study on (S)-4-methylhexyl-4-[4-(decyloxy)phenylethynyl]-2-fluorobenzate (MDOPEFB; Figure 1) in the chiral smectic C (Sc*) phase are reported. This compound will probably find some remarkable applications in the next decade because it forms the Sc* phase at room temperature and shows interesting properties on graphite surface [8]. For this study an asynchronous time-resolved FT-IR method which does not require any modifications in either the hardware or the software of the existing spectrophotometer is applied [7,9]. In this method, in principle, there is no shortest time limit for measured phenomena and, with the use of the MCT detector, a 10^{-6} second (1 μs) time resolution

can be achieved. Moreover, it was shown that this method allows one to measure with high accuracy both broad and sharp bands, maintaining all the advantages of FT-IR spectrometry [7]. By using this method the time course studies for the effects of the temperature and voltage of the electric field applied become possible and the mechanism of reorientation of the FLC molecule can be discussed. This is the first investigation in these effects performed on the molecular segment level.

EXPERIMENTAL

The sample of MDOPEFB was synthesized at Sanyo Chemical Industries, Ltd [10]. The polarized infrared spectra were recorded at 4 cm^{-1} resolution on a JEOL JIR 6500 FT-IR spectrophotometer equipped with a micro-attachment (JEOL IR-MAU 110) and MCT detector. One hundred scans were accumulated to ensure an acceptable signal-to-noise ratio. The FT-Raman spectrum was recorded on a JEOL JRS-FT 6500N FT-Raman spectrophotometer. For the time-resolved measurements a boxcar integrator (Stanford Research Systems; SR 250) with the gate width of 10 μs was applied. Figure 2 shows a block diagram of the asynchronous time-resolved FT-IR spectrophotometer employed for this study. The reorientation of the sample was induced by rectangular electric pulses of ± 5-28 V and 1.0 kHz frequency arising from a function generator (KENWOOD; FG-273) and self-made linear amplifier. To construct the LC cell BaF_2 windows covered with a thin layer of transparent conductive material (ITO) were used; they served as electrodes. Afterthen, a poly(vinyl alcohol) (PVA) film was deposited on the surface of the windows and was rubbed in one direction in order to induce the homogeneous orientation of the sample along the rubbing direction. The windows were separated by poly(ethylene terephthalate) (PET) spacers, and the pathlength calculated from the interference fringes of the empty cell was found to be 3.2 μm. The polarization axis of infrared line was fixed at 45° to the rubbing direction in order to get the largest changes in band intensities. A cross sectional diagram and a top view of the LC cell with respect to the polarized infrared line were illustrated in Figures 3 and 4, respectively. The cell was put into a

temperature control unit consisting of an OMRON E5T thermocontroller and Peltier-element. The accuracy of this unit is at least ± 0.1 °C. The sample was heated to the isotropic liquid state and then slowly (*ca.* 1.0 $Kmin^{-1}$) cooled down. The experiment was carried out at temperature of 14-32 °C, where the sample exists in the Sc* phase, and covered a time scale from 0 to 500 μs with intervals of 50 μs.

RESULTS AND DISCUSSION

Assignments of the Bands of Infrared Spectra of MDOPEFB

Figure 5 compares the FT-IR and FT-Raman spectra of MDOPEFB in the solid state, while in Figure 6 is shown the polarized infrared spectra of the sample in the cell for parallel (a), 45° (b), and perpendicular (c) polarization of the light with regard to the rubbing direction, respectively. Analyzing these spectra, the band assignments for selected bands and calculation of the dichroic rations were performed; the results are collected in Table I. For most of the bands one can observe a large intensity change upon changing the polarization. The calculated values of dichroic ratios distinctly differ from unity and, for a few of the bands, are larger than two; on the basis of this observation it is concluded that the degree of orientational order of the sample in the LC phase is very high.

The molecule of MDOPEFB consists of a grid core and two hydrocarbon chains The reorientation of the core may be examined by analysis of the intensity changes in the A-type bands (Table I), whereas those of the hydrocarbon chains can be investigated by use of the B-type bands. Unfortunately, the bands due to vibrations of the hydrocarbon chains (B-type) are not so strong and sharp as the bands due to vibrations of the core (A-type), except for the C-H stretching bands (2900 cm^{-1}) --- which are quite strong but, in turn, heavily overlap each other and form a very broad band contour, making it rather difficult to precisely investigate their intensity changes.

Time-Resolved FT-IR Spectra of MDOPEFB

In Figure 7, 8, and 9 are shown the time-resolved spectra of MDOPEFB for times of delay ranging from 0 to 500 μs measured at 14, 25, and 30 °C, respectively. The spectra represent the absorbance change from the spectrum of zero time delay. In making an LC cell, I have to compromise between a few important factors. The use of a thicker cell pathlength ensures a higher signal-to-noise ratio and reduces the possibility of a short circuit between cell windows. On the other hand, in a thick cell some of the bands may be too intense of their absorption; moreover, it is difficult to obtain domains that are large enough for time-resolved experiments. The molecules of the sample are well aligned in certain domains; however, this alignment may slightly differ from one domains to another. For that reason the time-resolved measurements should be carried out with the use of one well-oriented domain. There are no rigid rules, and the optimal cell thickness for each sample must have been chosen individually [11-13]. With the application of a micro-attachment, we could localized one large domain and then restrict the experiment to this domain area only. The intensity changes in most of the bands were clear and easily observable.

With regard to the response of the band to the electric field, one may divide bands into two types (Table I): type 1, which are upwards peaks, representing an increase in the intensity during the reorientation; and type 2 which are downwards peaks, showing a decrease in the intensity during change of the orientation. Assuming that the molecular axes are predominantly parallel toward the rubbing direction (without an electric field), one can conclude that the modes which have their transition

moments in the plane of the core belong to type 1, and those with transition moments perpendicular to the plane of the core belong to type 2. A schematic illustration for the reorientation of the FLC molecule with respect to the polarized infrared line is shown in Figure 4.

Features at 2922 and 2850 cm^{-1} are assigned to CH_2 antisymmetric and symmetric stretching modes of the hydrocarbon chains, respectively, which have transition moments perpendicular to the long axis of the molecule. A band due to a stretching mode of C≡C in the core part appears at 2212 cm^{-1}, while bands at 1605 and 1516 cm^{-1} are assigned to the ring stretching modes of the tolane ring. The directions of the transition moments of these modes are parallel to the long axis of core part of the molecule. As the time increases, the intensities of the bands due to the vibrations of the hydrocarbon chains decrease, while those of the core part increase, indicating that the molecule reorients from a large angle to a small one with respect to the direction of polarized infrared light. Analyzing Figures 7, 8, and 9, the change of orientation occurs immediately after the electric field is applied. Further detailed discussions of the rate of the reorientation for each part of the FLC will be described later.

The time-resolved spectra show one interesting feature: the carbonyl band (C=O stretch), which is usually strong in the infrared spectrum, is very weak in the time-resolved spectra. This result indicates that the bond between the benzene ring and carbonyl group rotates freely, so that the averaged absorbance of the band in the polarized infrared changes little in the time-resolved spectra.

Temperature Dependence of the Reorientation of MDOPEFB

Comparing Figures 7-9, it can easily be noticed that the intensity of the absorbance changes of the bands obviously depends upon the temperature of the LC cell. As the temperature increases, the intensity change of each band decreases. It seems likely that the tilt angle of the reorientation of the molecule deceases in the high temperature region of the Sc* phase. Figure 10 compares the TRFTIR spectra of 500 μs of delay measured at 14, 20, and 25 °C. The bands due to the hydrocarbon chains clearly appear in the spectrum at 14 °C. Compared with the spectrum measured at lower temperature, those bands in the spectra at higher temperatures shift toward high frequency and their intensities decrease. It seems therefore that the structure of the hydrocarbon chains becomes flexible with the increase of the temperature.

Figure 11 shows a variance of the absorbance change of the band at near 1286 cm^{-1}, assignable to a C-O-C antisymmetric stretching mode, in the temperature range of 14 to 30 °C. The rate of the increasing of the delta absorbance in the time region of 0-50 μs change a little with temperature, while the intensity at 500-μs delay time depends upon the temperature. Thus, it may be concluded that the temperature of the FLC does not influence upon in the angular velocity of reorientation, while the tilt angle is altered by the temperature. The absorbance changes below 25 °C indicate that the LC molecule does not finish up the reorientation within 500 μs, although the most of FLC reorient in a couple of hundreds micro-seconds time scale.

In Figure 12 (A) and (B) are shown the absorbance changes for 4

major bands measured at 14 and 30 °C, respectively, while Figure 13 illustrates the absorbance changes with normalized by their magnitudes in the spectra at 500 μs. The absorption bands due to the vibrations both of the core part (A-type) and the hydrocarbon chains (B-type) of MDOPEFB are clearly observable even for the 50-μs time period. This result suggests that, in principle, the molecule reorients as a unit; instead of an expectation that the core is more sensitive to the electric field than the hydrocarbon chains and needs a shorter period of time for the reorientation. When an electric field was applied to the LC cell, the dominant mechanism is an interaction of the electric field with anisotropy in the dielectric tensor of the sample in the LC state [1,2]. The anisotropy in the dielectric tensor is mainly due to the polar properties of the core. Assuming this theory, the rigid core of the molecule may start the reorientation first, and then the hydrocarbon chains follow the core. The results of this investigation, however, show that whole of the molecule reorients as though the FLC molecule were a rigid rod. In both temperature the intensity changes of these bands are similar to each other, indicating that the FLC molecule reorients as a unit irrespective of the temperature.

Dependence of the Reorientation of MDOPEFB on Magnitude of Electric-Field

Figures 14 and 15 show the TRFTIR spectra of the FLC measured at the temperature of 30 °C and the voltages of the electric-field of ± 9 and ± 28 V, respectively. The spectra obtained at high voltage are considerably intense compared with those at low voltage. The variance

of the absorbance changes of the band at near 1286 cm^{-1} is illustrated in Figure 16. It is clearly noticed that the reorientation does not finish within 500 μs in the voltages below ± 12 V. Moreover, the rate of the reorientation at the time delay region of 0-50 μs depends upon the magnitude of the electric-field induced. On the other hand, the intensity of the delta absorbance at 500 μs in the voltages over ± 20 V is very similar, indicating that the voltage of electric-field alters little the tilt angle of the reorientation. Although the maxima of the absorbance changes for the case of below ± 12 V cannot be determined because of the limitation of the interval of repetition for this time-resolved technique, it is easy to expect that they might be reach to similar tilt angle of the reorientation.

Figure 17 indicates the absorbance changes of the major bands measured at temperature of 30 °C with the applied voltages of ± 12V (A) and ± 28V (B), while Figure 18 presents their normalized absorbance changes. In both voltages the intensity changes of these bands resemble each other again, indicating that the FLC molecule reorients as a unit irrespective of the magnitude of voltage of electric field.

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Table I. Vibrational band assignments for MDOPEFB.

Wavenumber/cm^{-1}	Assignment	Dichroic ratio*	Type
2954	CH_3 asym. stretch.	0.9	B2
2922	CH_2 asym. stretch.	0.8	B2
2848	CH_2 sym. stretch.	2.3	B2
2208	C≡C stretch.	1.9	A1
1710	C=O stretch.	0.4	A2
1616	ring C-C stretch.	1.1	A1
1603	ring C-C stretch.	2.2	A1
1514	ring C-C stretch.	1.8	A1
1466	CH_2 asym. bend.	3.6	B1
1281	ring-C-O stretch.	1.5	A1
1242	ring-O stretch.	1.3	A1
1209	ring-F stretch.	1.5	A2
1172	ring-O-C stretch.	3.9	A1
1135	O-CH_2 stretch. (ester)	-	B1
1126	chain C-C stretch.	0.8	B1
1080	ring C-C def.+sym. strech.	-	A1
1018	C-H bend. (ring) in-plane	-	A1
874	ring CH out-of-plane def.	1.7	A2
831	ring CH out-of-plane def.	2.2	A2
812	ring CH out-of-plane def.	1.9	A2

A - modes due to vibrations of the core

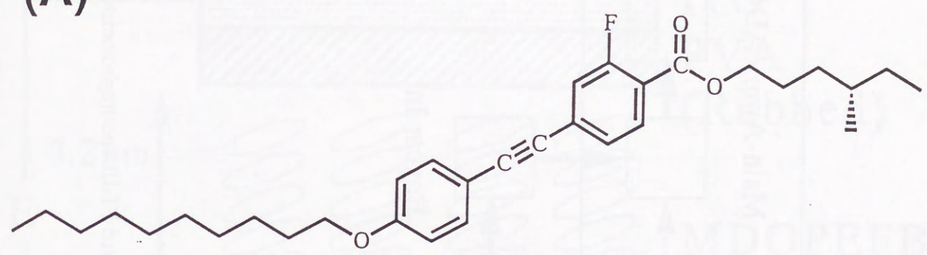
B - modes due to vibrations of the hydrocarbon chains

1 - modes with transition moments in parallel with the core

2 - modes with transition moments perpendicular to the core

* - the values are only approximated because of the heavily overlap.

(A)



(B)

$$\mathrm{Cr} \underset{-2.8\ ^{\circ}\mathrm{C}}{\overset{18.2\ ^{\circ}\mathrm{C}}{\rightleftharpoons}} \mathrm{Sc}^{*} \underset{37.7\ ^{\circ}\mathrm{C}}{\overset{38.2\ ^{\circ}\mathrm{C}}{\rightleftharpoons}} \mathrm{S_A} \underset{46.5\ ^{\circ}\mathrm{C}}{\overset{47.5\ ^{\circ}\mathrm{C}}{\rightleftharpoons}} \mathrm{I}$$

Figure 1. (A) The molecular structure of (S)-4-methylhexyl-4-[4-(decyloxy)phenyl ethyl]-2-fluorobenzate (MDOPEFB). (B) Phase sequence of MDOPEFB.

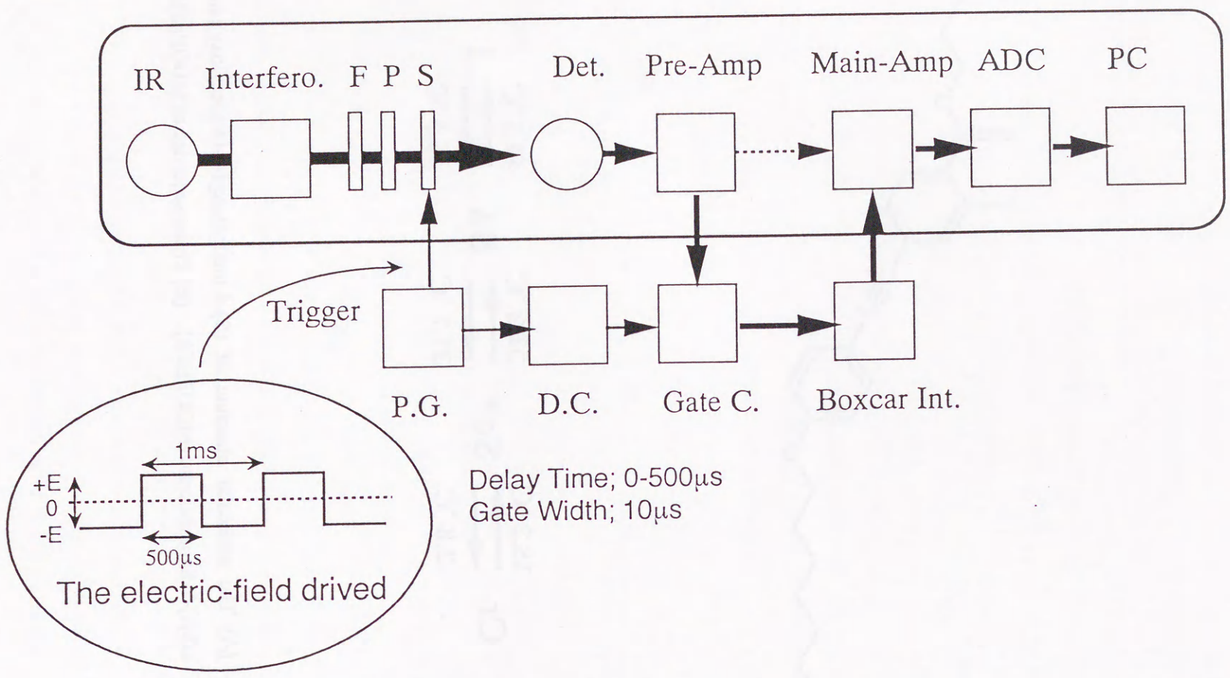


Figure 2. Block diagram of the asynchronous time-resolved FT-IR spectrophotometer and the electric-field driven in this study.

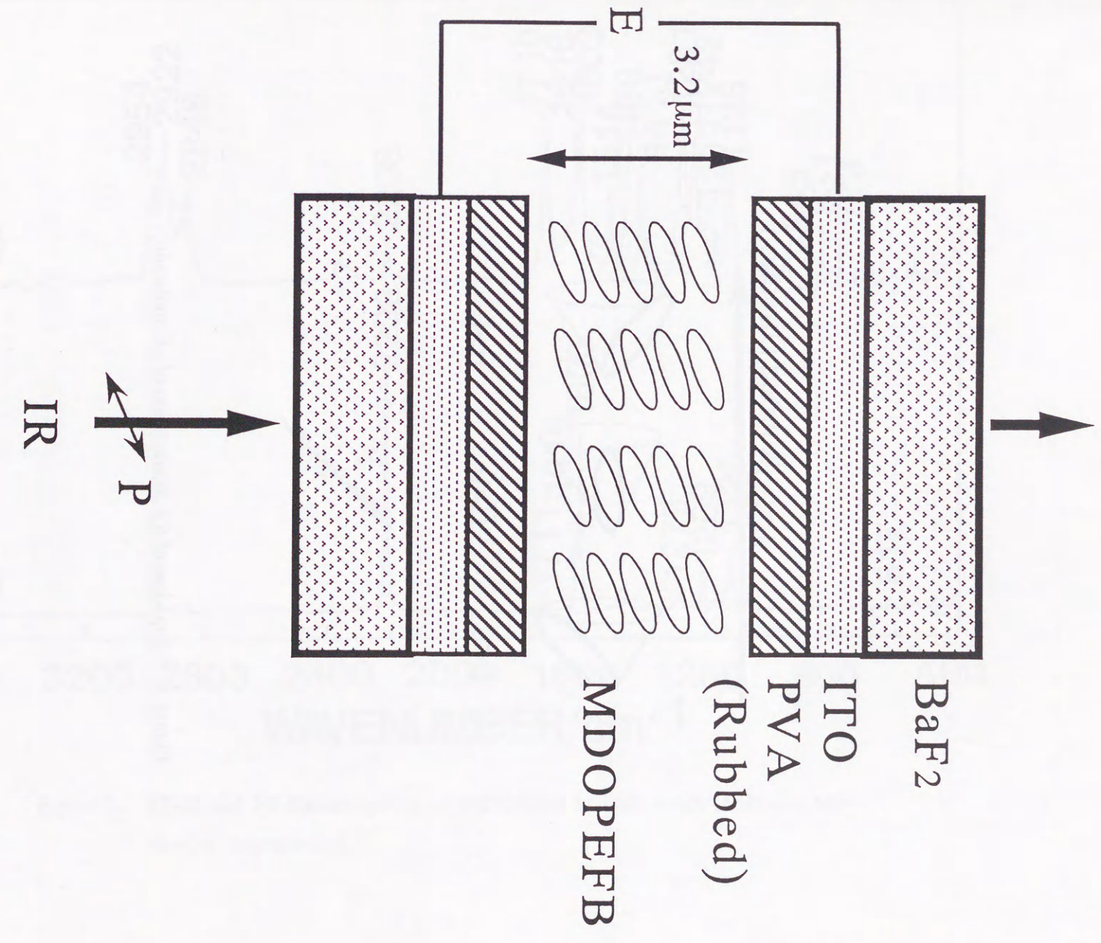


Figure 3. Schematic illustration of the LC cell employed.

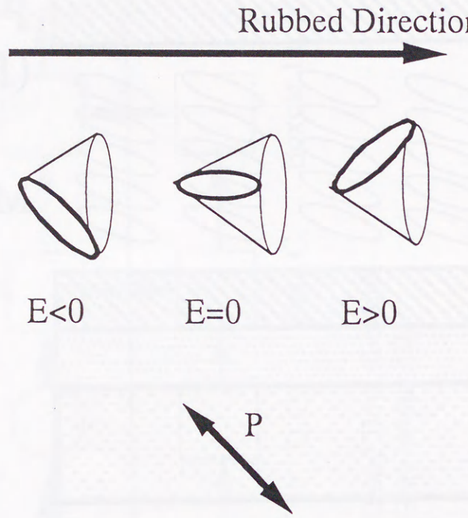


Figure 4. Top view of the reorientation of LC molecule.

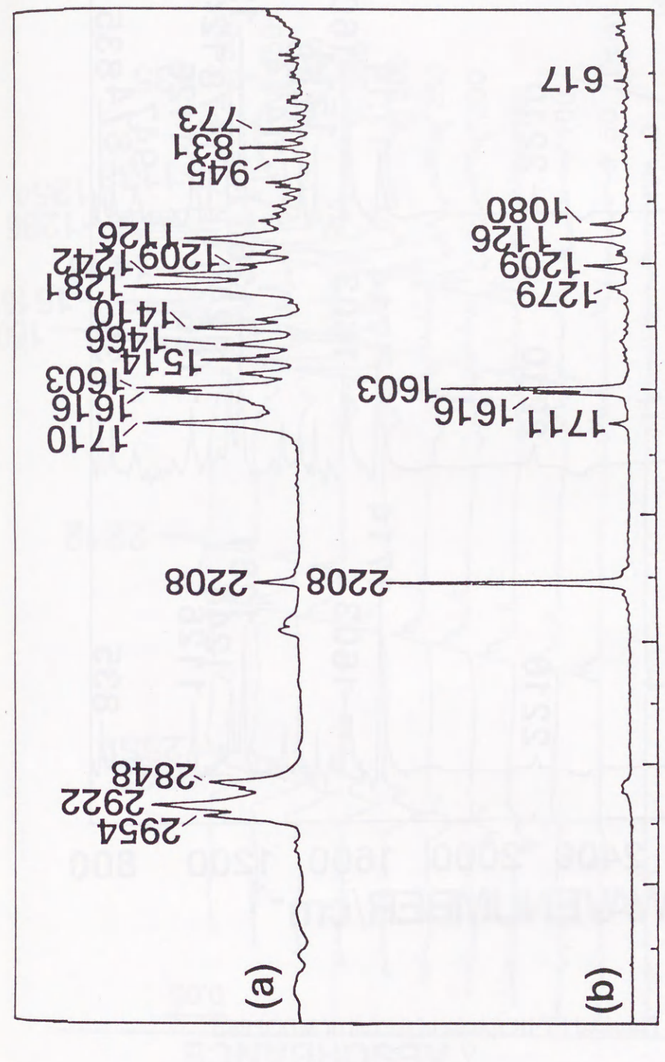


Figure 5. FT-IR and FT-Raman spectra of MDOPEFB in bulk states (KBr disc and powder, respectively).

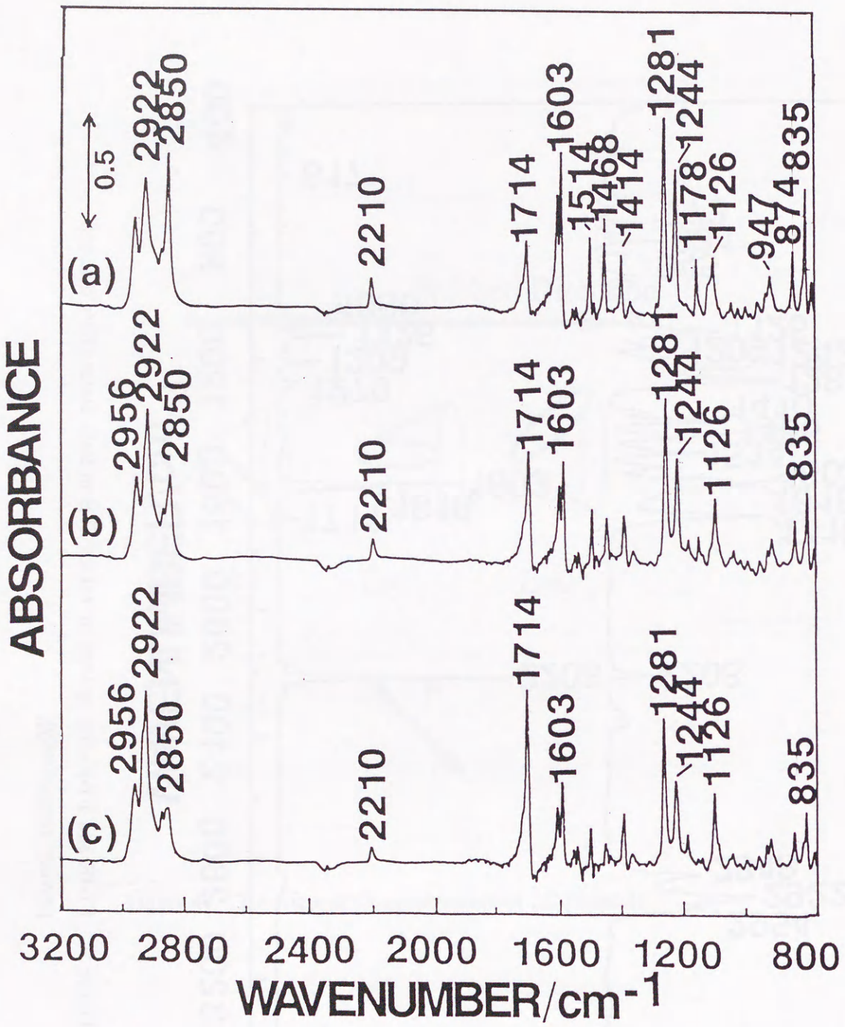


Figure 6. Polarized FT-IR spectra of the cell of MDOPEFB.

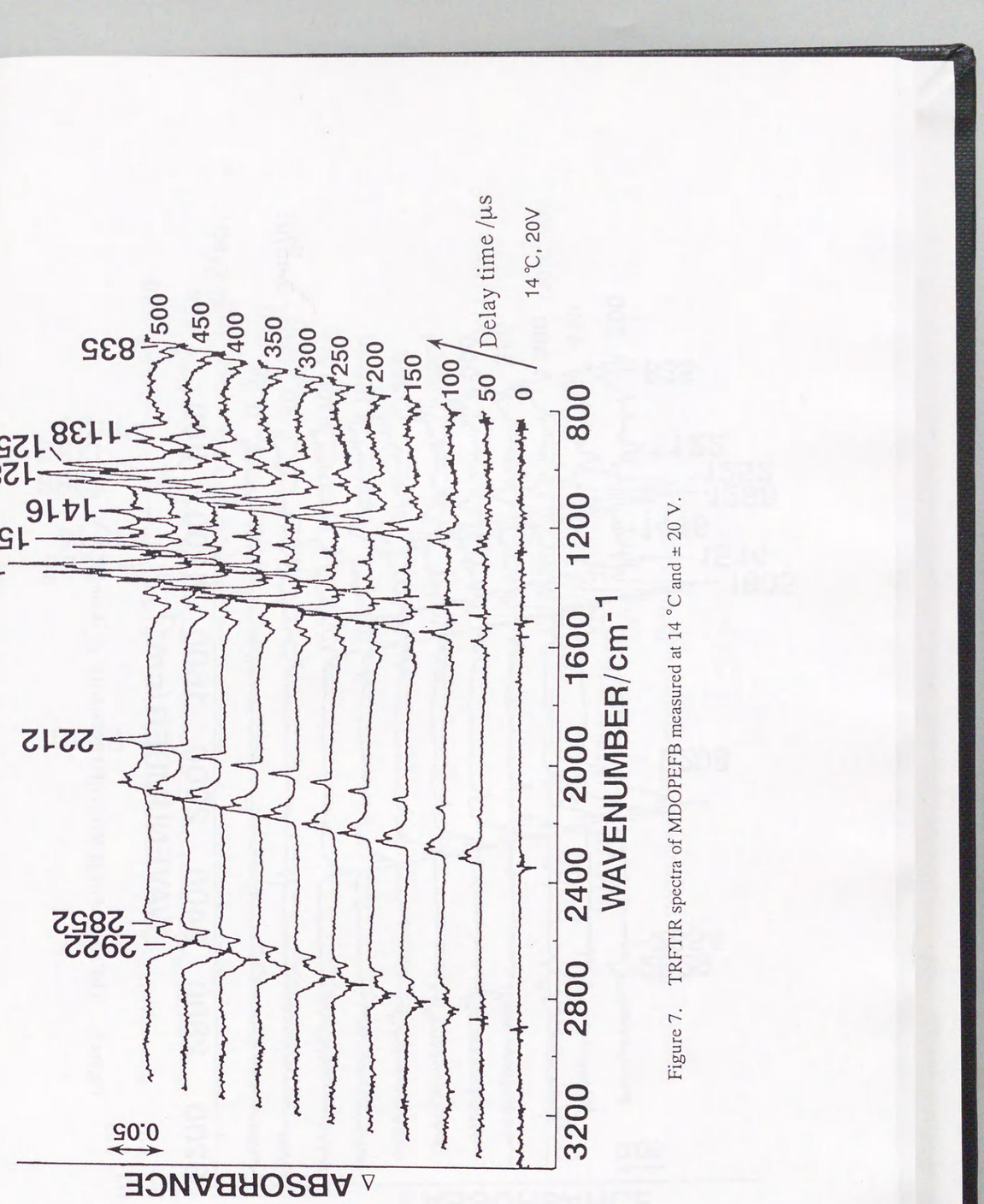


Figure 7. TRFTIR spectra of MDOPEFB measured at 14 °C and ± 20 V.

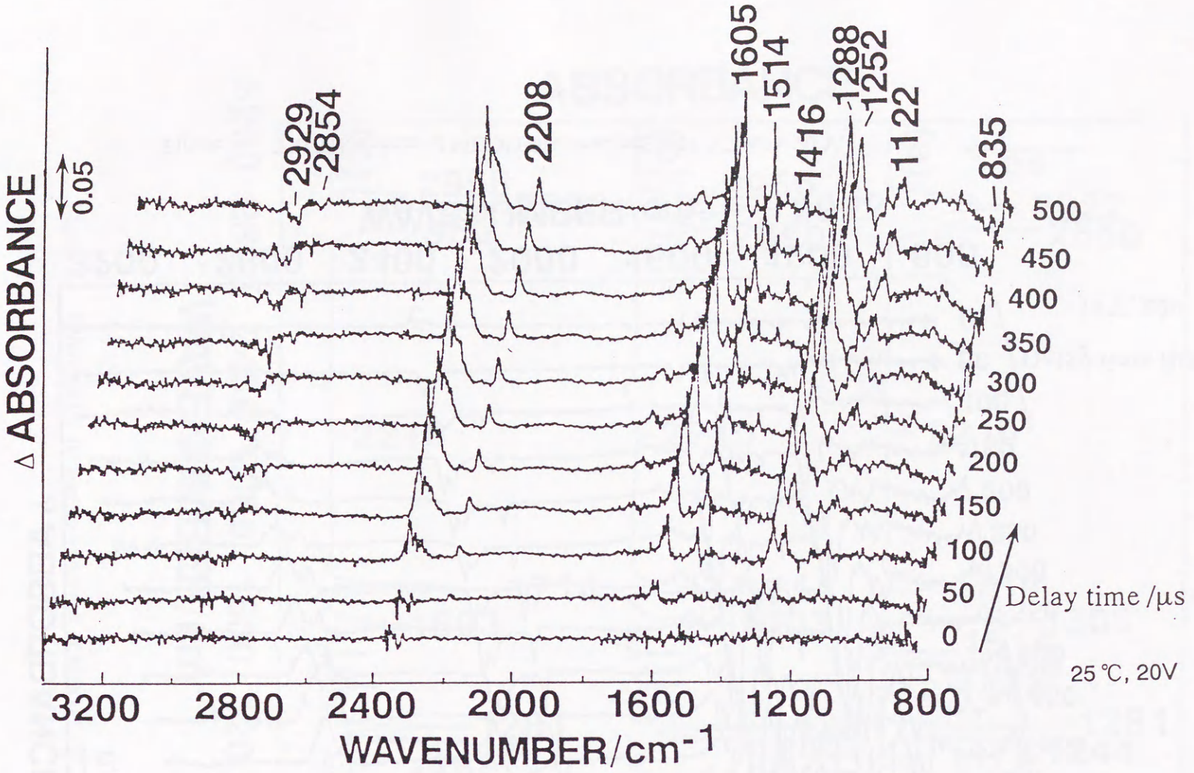


Figure 8. TRFTIR spectra of MDOPEFB measured at 25 °C and ± 20 V.

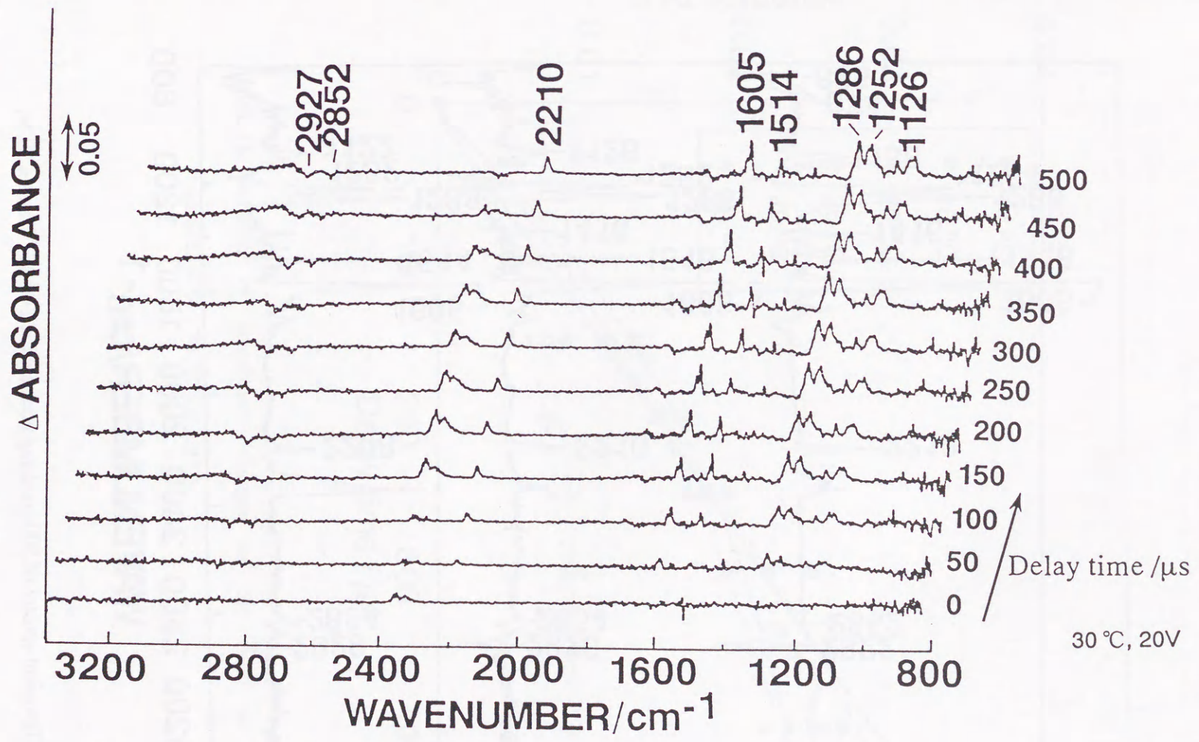


Figure 9. TRFTIR spectra of MDOPEFB measured at 30 °C and ± 20 V.

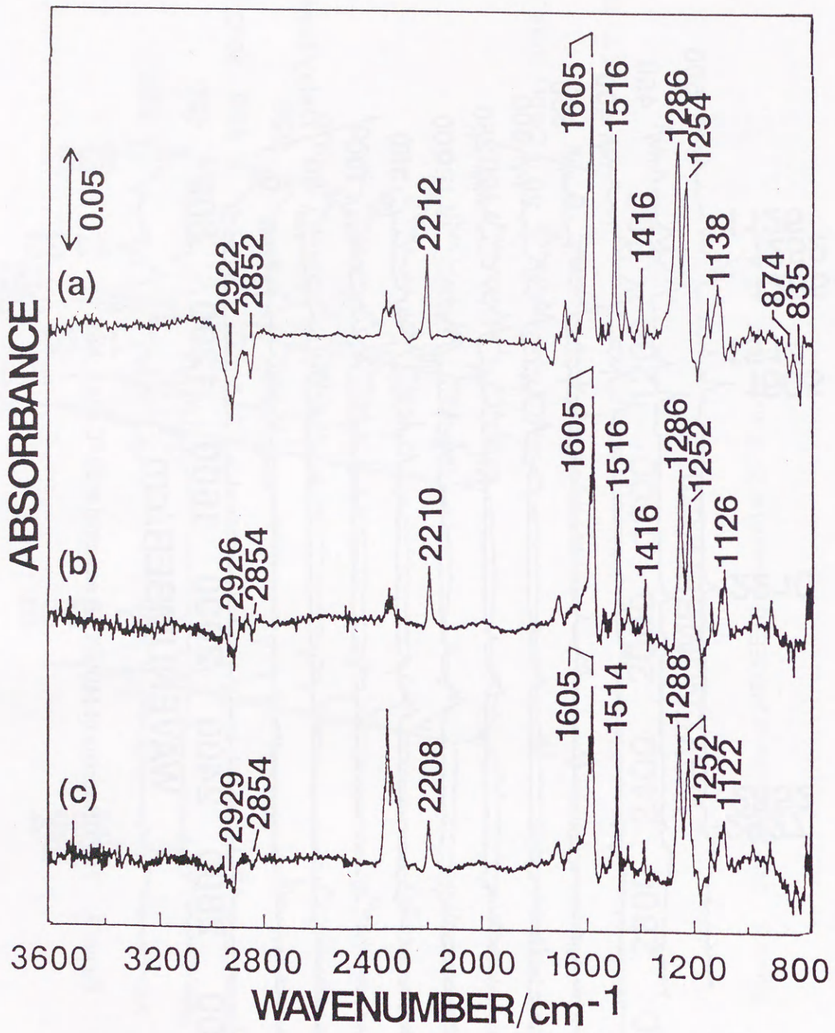


Figure 10. Transient spectra of 500-μs delay measured at 14 - 25 °C and ± 20 V.

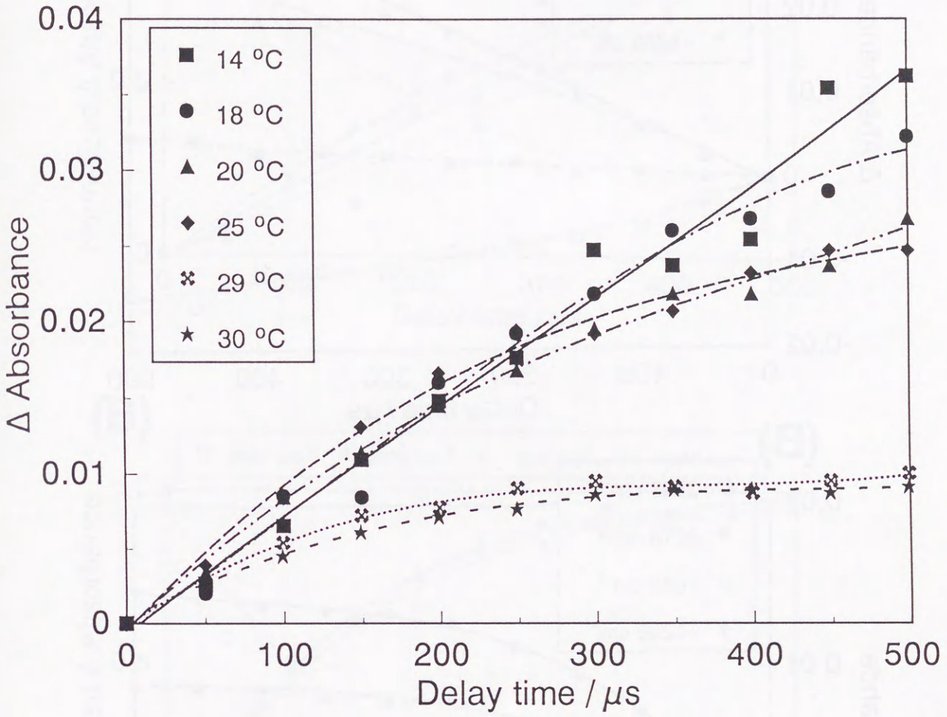


Figure 11. Variance of absorbance changes of the band at ~1286 cm^{-1} measured at 14 - 30 °C and ± 20 V.

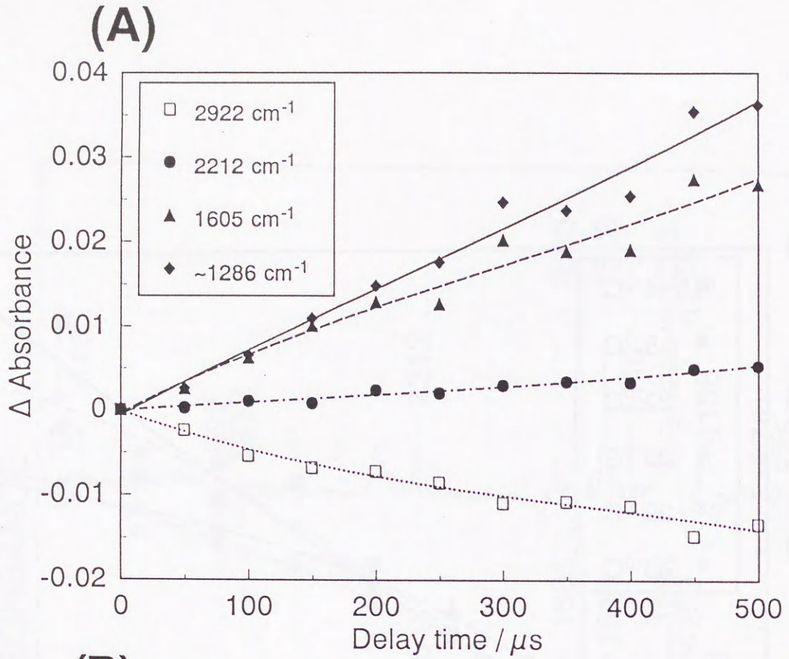
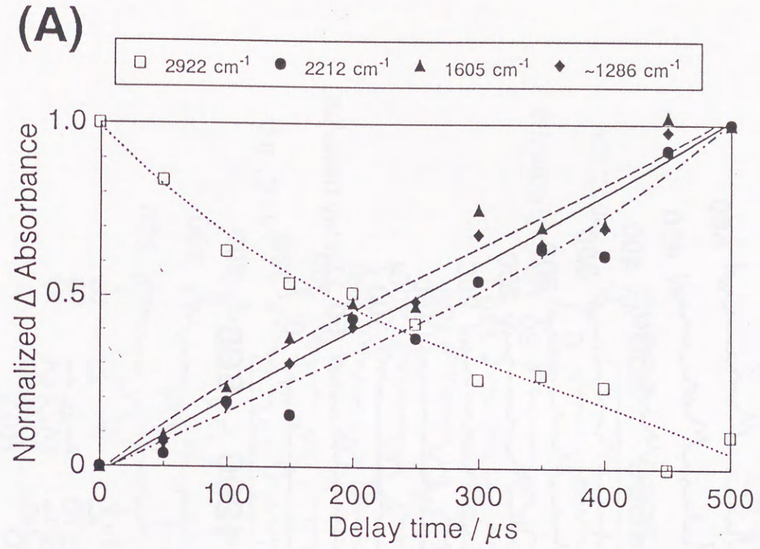


Figure 12. Variance of absorbance changes of the major bands measured at 14 °C (A) and 30 °C (B). The voltage of ± 20 V was employed.



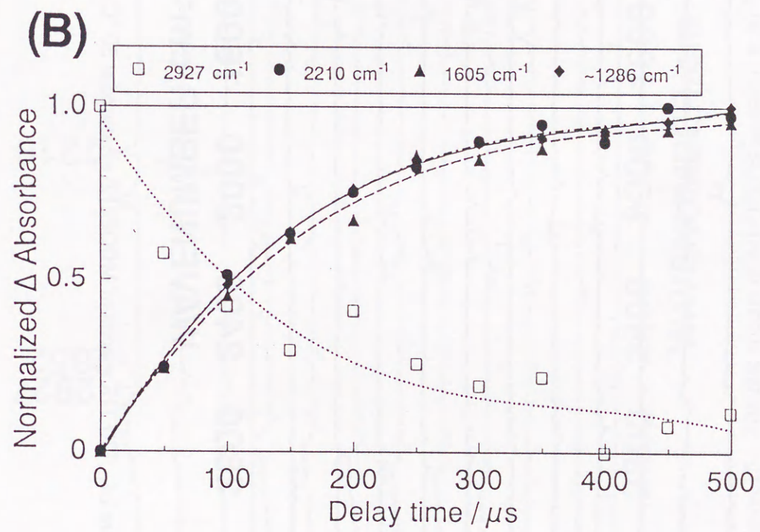


Figure 13. Comparison of normalized absorbance changes of the major bands measured at 14 °C (A) and 30 °C (B). The voltage of ± 20 V was employed.

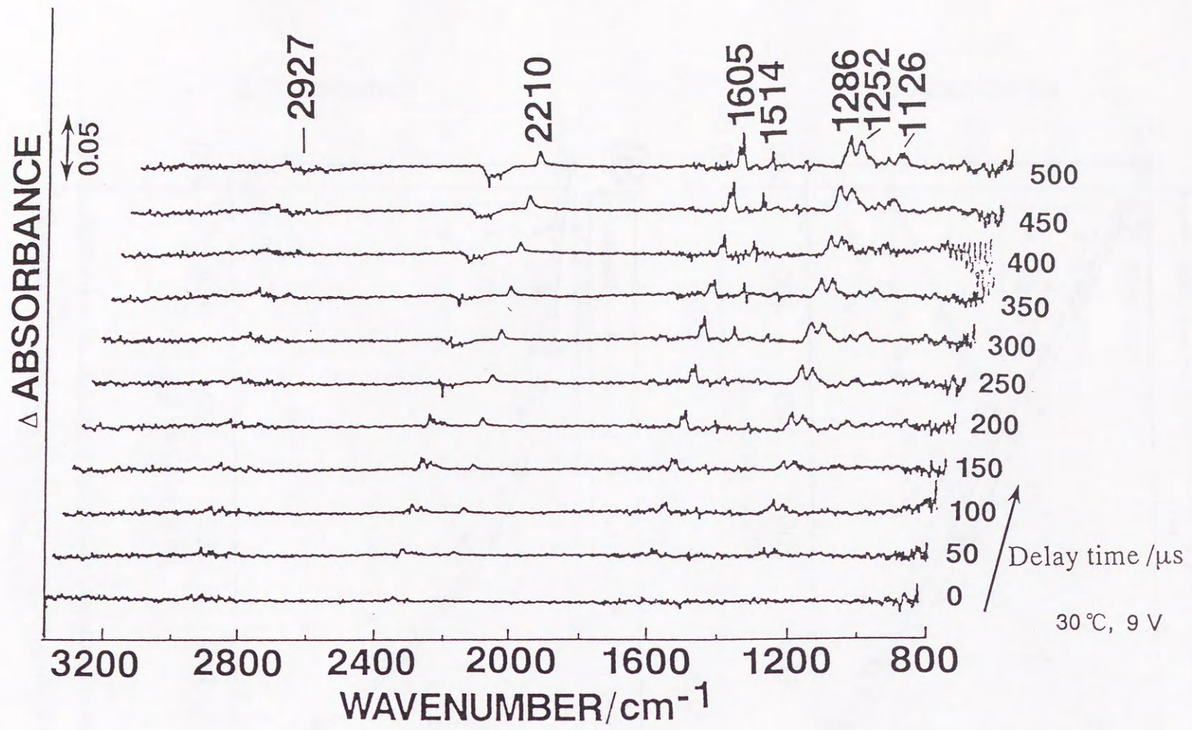


Figure 14. TRFTIR spectra of MDOPEFB measured at 30 °C and ± 9 V.

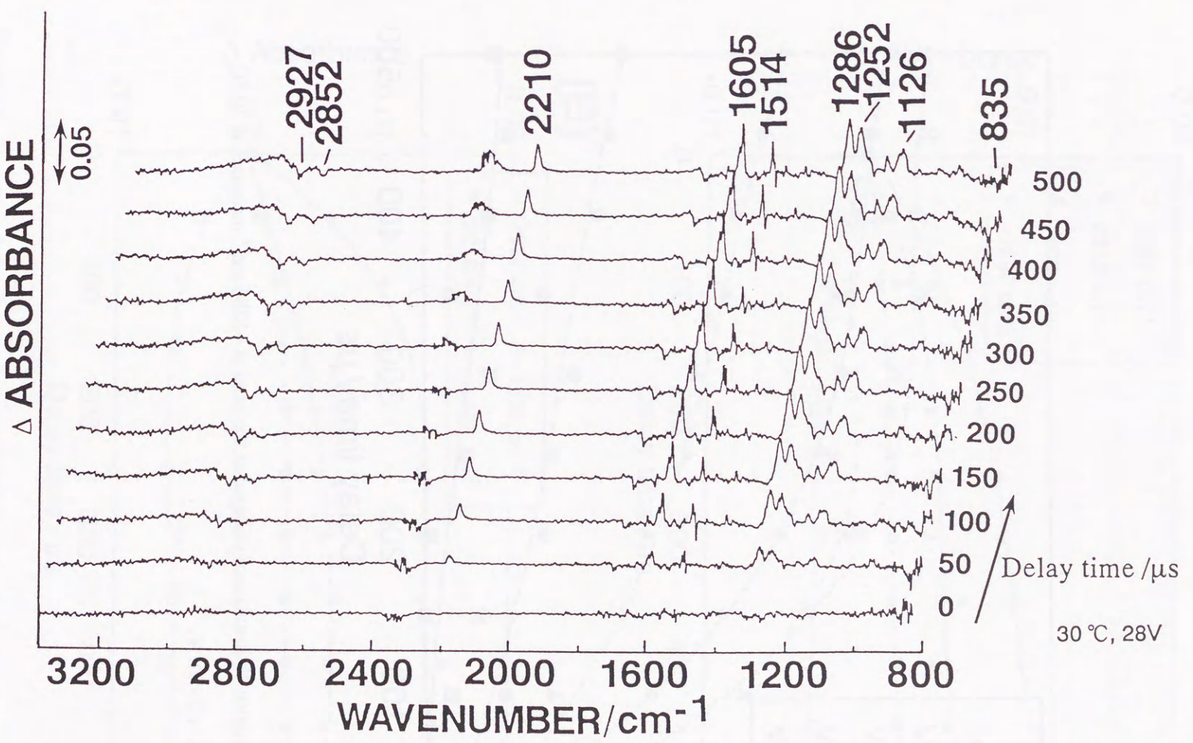


Figure 15. TRFTIR spectra of MDOPEFB measured at 30 °C and ± 28 V.

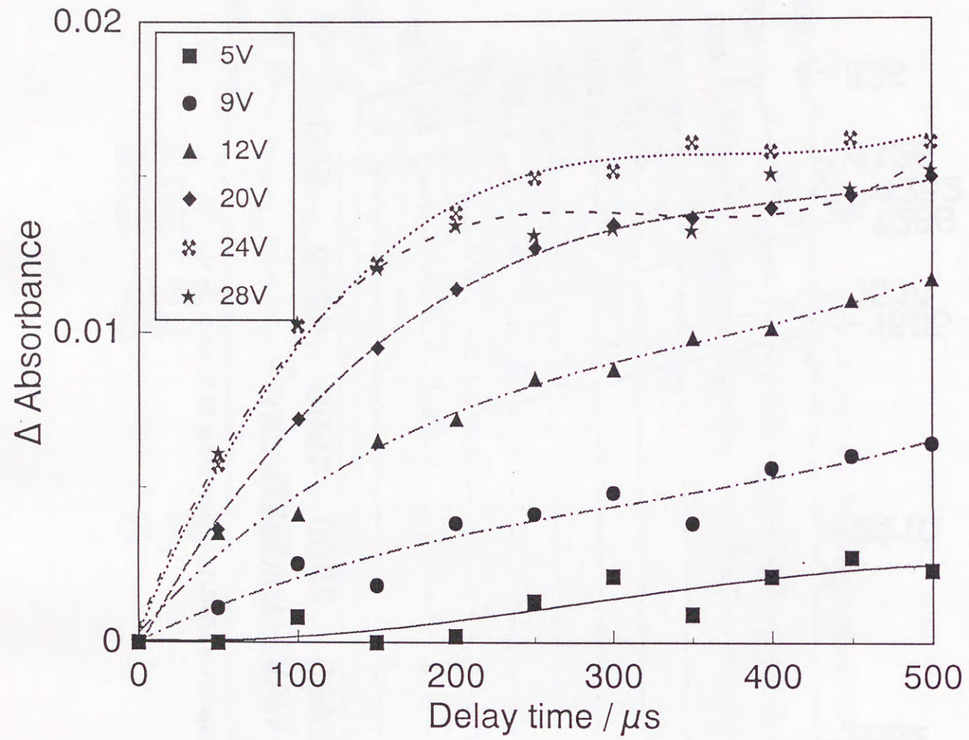


Figure 16. Variance of absorbance changes of the band at ~1286 cm^{-1} measured at 30 °C and ± 5 - 28 V.

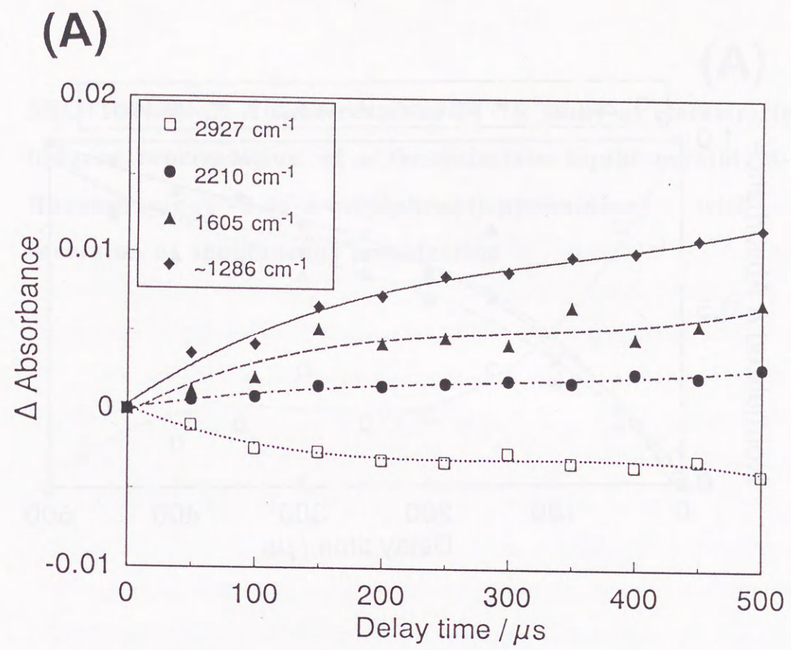
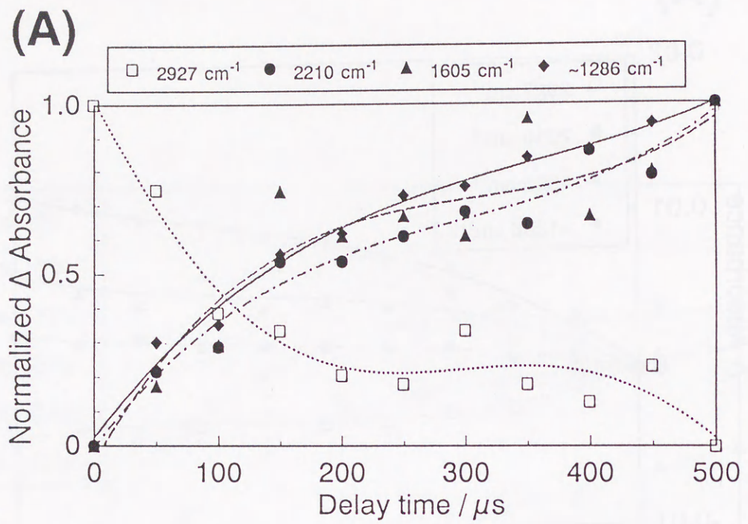


Figure 17. Variance of absorbance changes of the major bands measured at ± 12 (A) and ± 28 V (B). The temperature at 30 °C was employed.



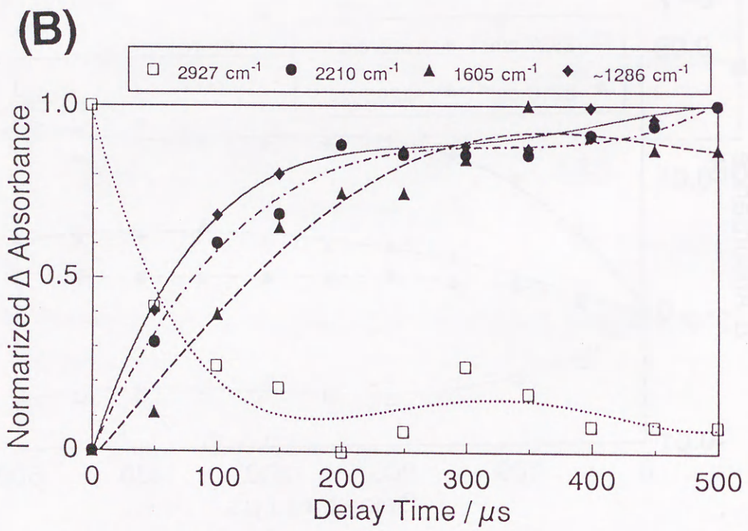


Figure 18. Comparison of normalized absorbance changes of the major bands measured and ± 12 V (A) and ± 28 V (B). The temperature at 30 °C was employed.

SECTION III-2: A time-resolved FT-IR study of electric-field-induced reorientation of a ferroelectric liquid crystal, 5-(2-fluorooctyloxy)-2-(4-*n*-octylphenyl)-pyrimidine, with an inversion of spontaneous polarization

ABSTRACT

The electric-field-induced reorientation of the smectic C* phase of 5-(2-fluorooctyloxy)-2-(4-*n*-octylphenyl)-pyrimidine was investigated by using an asynchronous time-resolved FT-IR technique. The time-resolved study indicates that the liquid crystal molecule reorients from perpendicular (zero time of delay) to parallel (500 μs delay) direction with respect to that of the polarized infrared light at 32 °C while it does reversely at 41 °C. It is also shown that the change in the voltage applied has little influence on the rate of reorientation in the region of the positive spontaneous polarization (Ps), while the rate in the region of the negative Ps strongly depends upon the voltage. These results suggest that the mechanism of the reorientation varies upon the Ps inversion. The absorbance changes for major bands are very similar to each other, indicating that the molecule reorients simultaneously as a unit.

INTRODUCTION

The mechanism of the reorientation of liquid crystals is still not well understood in spite of their wide applications [1,2]. In order to investigate it I have employed time-resolved Fourier transform infrared spectroscopy (TRFTIR) [3,4]. This technique enables one to obtain information about the motion of the whole molecule as well as details of the time course of the reorientation of particular fragments of the molecule [3,5,6].

Following the previous section, another TRFTIR study of a ferroelectric liquid crystal (FLC) was presented in this section. A novel FLC, 5-(2-fluorooctyloxy)-2-(4-*n*-octylphenyl)-pyrimidine (8BPyO8(2F)*; Figure 1), which shows an inversion of the spontaneous polarization (Ps) (shown in Figure 2) with temperature change within the range of chiral smectic C phase (Sc*) [7], was selected for the present study. The mechanism of the Ps inversion in the above compound, which is rare phenomenon for FLCs, has never been discussed and predicated; the TRFTIR study may give some insight into the dynamics of the mechanism of the inversion.

EXPERIMENTAL

The FLC, 8BPyO8(2F)* was synthesized at Chisso Petrochemical Corporation, and generously donated [7]. It was placed between BaF_2 windows coated with rubbed poly(vinyl alcohol). The cell thickness was controlled by poly(ethylene terephthalate) spacers and found to be 3.5 μm. The cell was put into a temperature control unit described in previous section. The square wave with voltages ± 3-28 V and frequency 1.0 kHz from the function generator and linear amplifier was applied to the cell. To obtain a good domain of LC the cell was gradually cooled down from the isotropic phase.

The infrared spectra were recorded on a JIR6500 (JEOL) FT-IR spectrophotometer equipped with a micro attachment (JEOL IR-MAU 110) and a MCT detector. For time-resolved measurements a boxcar integrator (Stanford Research System; SR250) was used with the delay time of 0-500 μs and the gate width of 10 μs. The TRFTIR system employed was the asynchronous type [3,8] described in SECTION III-1. The scanning speed of interferometer was 0.6 mms^{-1} and the spectroscopic resolution was 8 cm^{-1}; 100 scans were accumulated for every measurement to ensure a good signal-to-noise ratio.

FT-Raman spectrum was measured with the same apparatus as that described in the previous section.

RESULTS AND DISCUSSION

Infrared Spectra of 8BPyO8(2F)*

Figure 3 shows a FT-IR (a) and FT-Raman (b) spectra of 8BPyO8(2F)* in a bulk state. A comparison of these spectra is helpful for the assignments of the bands in time-resolved infrared spectra. Bands at 2921 and 2850 cm^{-1} in the infrared spectrum are assigned to CH_2 antisymmetric and symmetric stretching modes of the hydrocarbon chains, respectively. Three medium intense bands at 1610, 1578, and 1549 cm^{-1} and one intense band at 1444 cm^{-1} are all due to ring stretching modes of phenylpyrimidine group, while a band at 1286 cm^{-1} is assigned to an antisymmetric stretching mode of the ring-O-C group [9]. A band at 1086 cm^{-1} may be due to a C-F stretching mode, and CH out-of-plane deformation modes of phenylpyrimidine group are identified near 856 cm^{-1} [9].

The compound 8BPyO8(2F)* has the phase transition S_A-Sc* at 45.0 °C, and shows reversible Ps within the temperature range of Sc*. (The sequence of phase transitions is listed in Figure 1.) Figure 4, 5A, and 5B display the polarized FT-IR spectra of the LC cell of the sample measured at 34, 40, and 52 °C, respectively. These spectra indicate that the degree of orientational order of the LC cell was very high. Moreover, the orientation of the sample without the electric-field-induction is almost the same among Sc* phase in the positive (34 °C) and negative (40 °C) Ps, and S_A phase (52 °C). This result suggests that the orientation predetermined by the interaction between the substrate surface and sample has no effect on changes of the Ps inversion of the sample.

In Figure 6 are shown TRFTIR spectra of 8BPyO8(2F)* measured at ± 3 V and 32 °C (*i.e.*, Ps>0). Each spectrum represents a difference between given spectrum and zero time of delay spectrum. Intensities of the bands at 1612 (rings), 1443 (rings), and 1286 (ring-O-C) cm^{-1}, whose vibrational modes have transition moments parallel to the long axis of the molecule, increase with increasing delay time, while those of the features near 2900 (CH_2), 1086 (C-F), 914 (C-H out-of-plane), and 856 (C-H out-of-plane) cm^{-1}, whose vibrational modes have perpendicular transition moments, decrease. These results suggest that the LC molecule reorients from perpendicular (0 μs) to parallel (500 μs) direction with respect to that of the polarized infrared light. Analyzing Figure 6 it can be easily noticed that the change of orientation occurs immediately after the electric field is applied.

Temperature and Voltage Dependencies of the Reorientation of 8BPyO8(2F)* in Time-Resolved Infrared Spectra

In Figure 7 and 8 are shown the TRFTIR spectra of the sample measured at 37 and 41 °C, respectively. The different spectra at 37 °C are almost flat throughout all delay time, indicating that the molecule does not reorient at this temperature, although the FLC takes the Sc* phase. It is easily concluded that the Ps is zero at this temperature, so that no reorientation occurs in spite of applying of electric field. On the other hand, all of the bands in the spectra at 41 °C appear in the opposite direction compared with those at 32 °C (Figure 6). It is well demonstrated that the direction of the reorientation of 8BPyO8(2F)* alters by the inversion of the sign of Ps; the LC molecule reorients from parallel to perpendicular direction at high temperatures (above 41 °C) although the same polarity of the electric field was applied. These

phenomena agree well with the results of Ps measurements (Figure 2).[3]

Figure 9 shows temperature dependency of the rate of reorientation. The ordinate represents the difference of integrated absorbance of the band at 1443 cm^{-1} (a ring stretching mode of phenylpyrimidine group) in the time-resolved difference spectra while the abscissa indicates the delay time. As described before, the direction of the reorientation inverses between the temperature below 36 °C and that above 41 °C. The reorientation finishes within a 300-μs time period throughout these temperature; the delta absorbance at 500 μs delay reflects the tilt angle of the FLC under each condition. A comparison of these curves suggests that the angular velocity of the reorientation depends upon the temperature; it becomes slower with increasing of temperature in the positive Ps region, while it becomes much faster in the negative Ps region.

In Figure 10 are compared transient spectra of 8BPyO8(2F)* for 500 μs delay measured at 32 (a), 35 (b), 37 (c), 41 (d), and 44 (e) °C, respectively. Note that the frequencies of bands in those spectra change little with temperature change. These results indicate that the structure of the 8BPyO8(2F)* is almost identical to each other in the above temperature range. The spectrum at 44 °C (e) is almost flat, indicating that the orientation of the molecules does not occur at this temperature; the temperature employed is so close to that of phase transition between S_A and Sc* that the tilt angle is nearly zero. In contrast, in the case of 37 °C (c), although the spectrum is also flat, it is due to the fact that the Ps is equal to zero inside of Sc* phase as described previously.

Plotting an integrated absorbance change normalized by the final intensity of each band (intensity at 500-μs delay), one can estimate the rate of reorientation of a group whose mode contributes to the band.

Figure 11 shows the normalized absorption changes for three major bands, the bands at 2927, 1443, and 1286 cm^{-1}, measured at 33 °C and 3 V. This result indicates that the core part and hydrocarbon chains move together to each other; the FLC molecule reorients simultaneously as a unit.

Figure 12A illustrates the voltage dependency of the rate of reorientation at the constant temperature of 32 °C. The magnitude of voltage applied was varied from ± 3 to ± 28 V. The rate of reorientation is almost unchanged at these voltages in contrast with a theoretical consideration [10], *i.e.*, the response time is proportional to electric field. Quite different behavior of the sample is observed at 41 °C (Ps<0); the corresponding graph is shown in Figure 12B. The rate of reorientation strongly depends upon voltage and at sufficiently high voltages becomes much faster than that one at 32 °C (Ps>0). These results suggest that the reorientation of the FLC is swayed by different mechanisms between the positive and negative Ps circumstances. This behavior was realized for the first time, and may give some information to understand the mechanisms both of the reorientation and Ps inversion.

In conclusion, the present study has demonstrated that TRFTIR technique is very powerful for investigating the electric-field-induced reorientation of 8BPyO8(2F)*.

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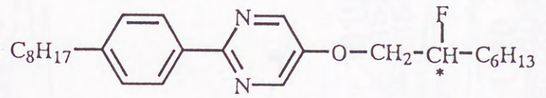
(A)



(B)

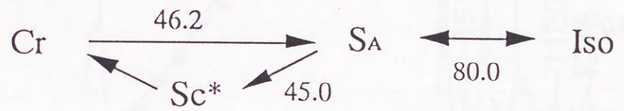


Figure 1. (A) The structure of 5-(2-fluorooctyloxy)-2-(4-*n*-octylphenyl)-pyrimidine; 8BPyO8(2F)*. (B) Phase transition of 8BPyO8(2F)*.

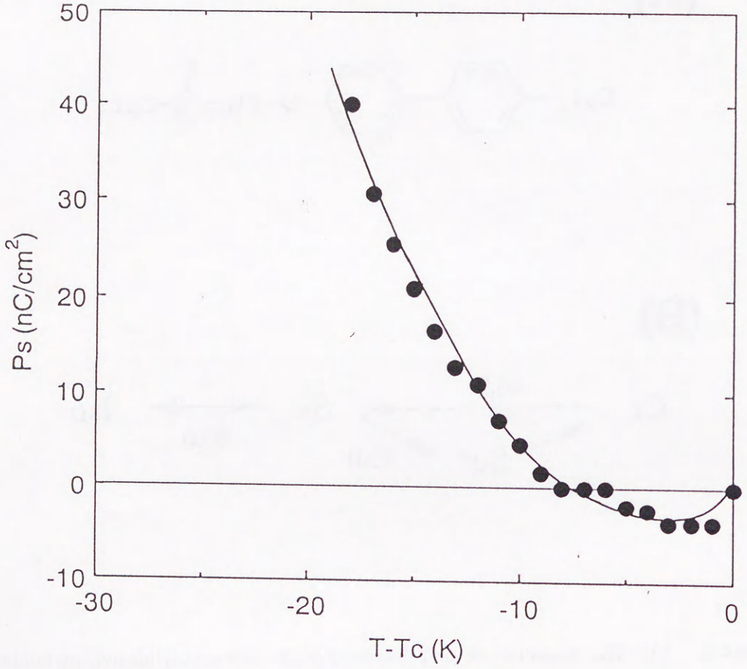


Figure 2. Variance of spontaneous polarization (Ps) of 8BPyO8(2F)*.

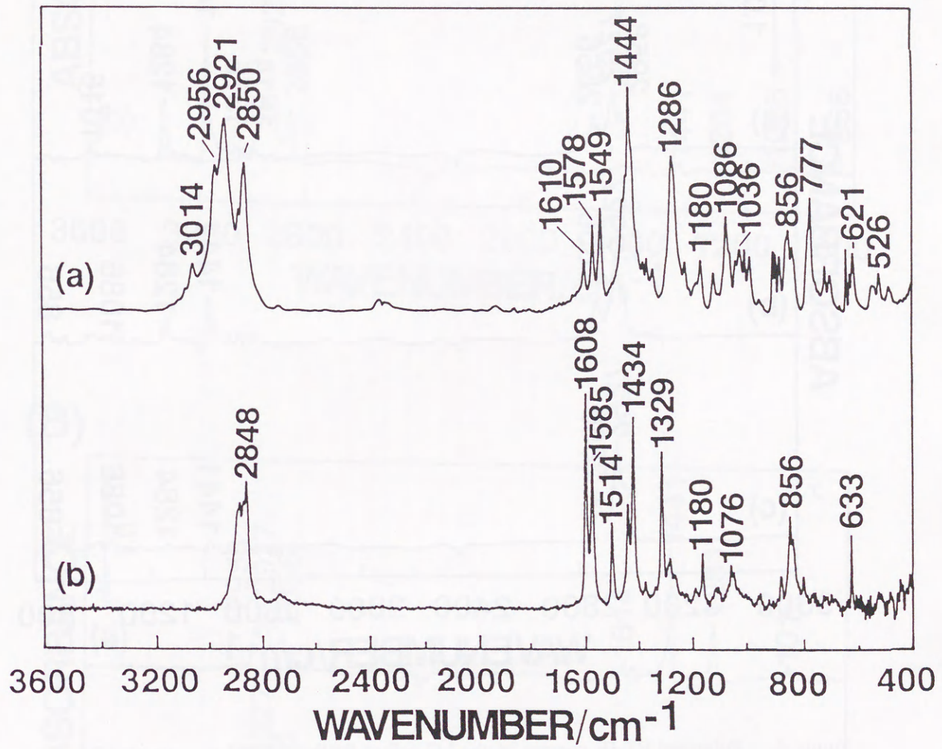


Figure 3. FT-IR (a) and FT-Raman (b) spectra of 8BPyO8(2F)* in bulk state.

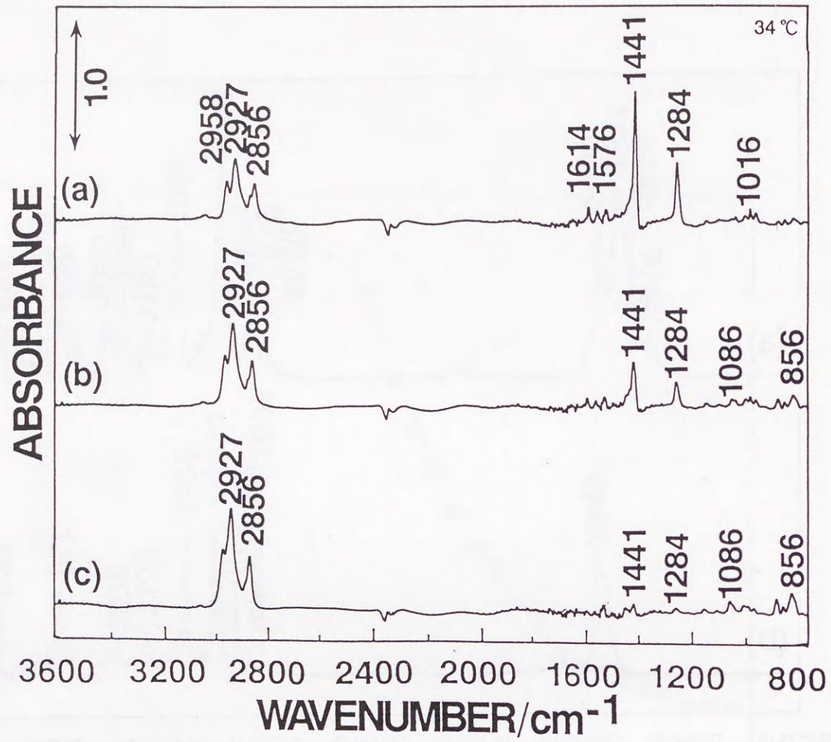
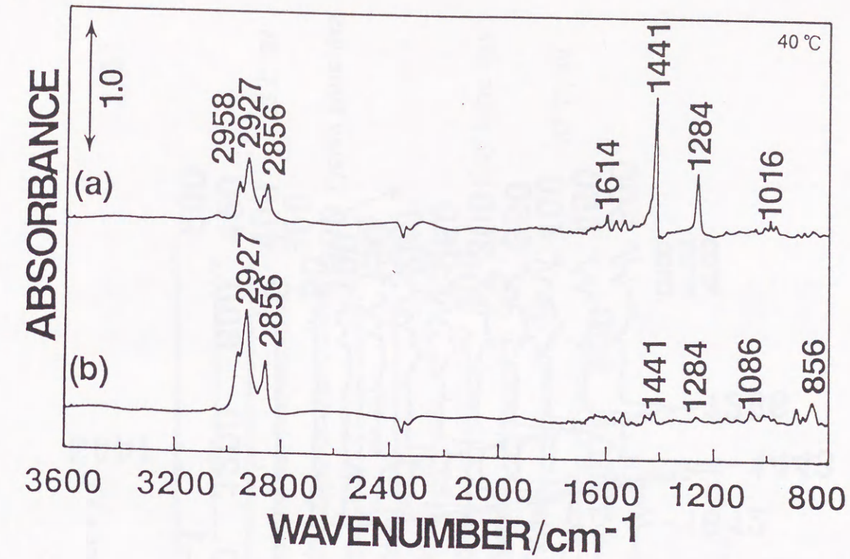


Figure 4. Polarized FT-IR spectra of the LC cell of 8BPyO8(2F)* measured at 34 °C. The angles of probe lights are 0°(a), 45°(b), and 90°(c) from the rubbing direction, respectively.

(A)



(B)

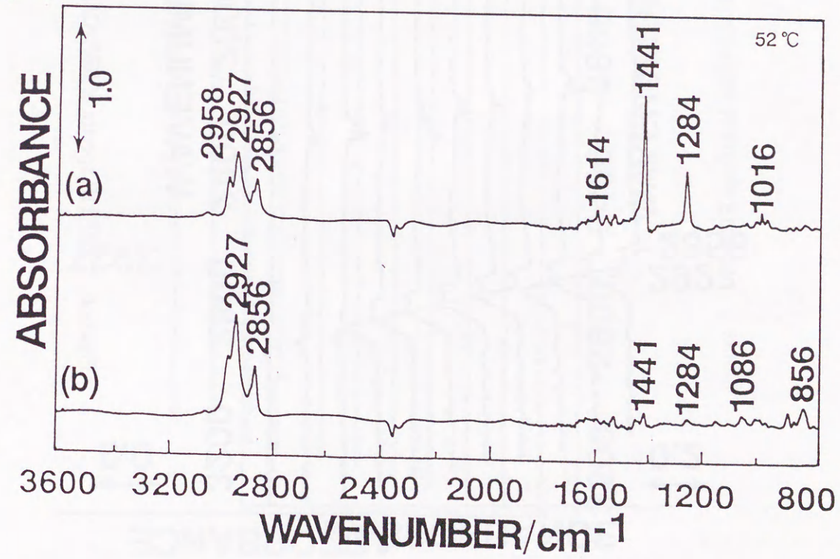


Figure 5. Polarized FT-IR spectra of the LC cell of 8BPyO8(2F)* measured at 40 °C (A) and 52 °C (B). Parallel (a) and perpendicular (b) lights with respect to the rubbing direction were employed to observe the spectra.

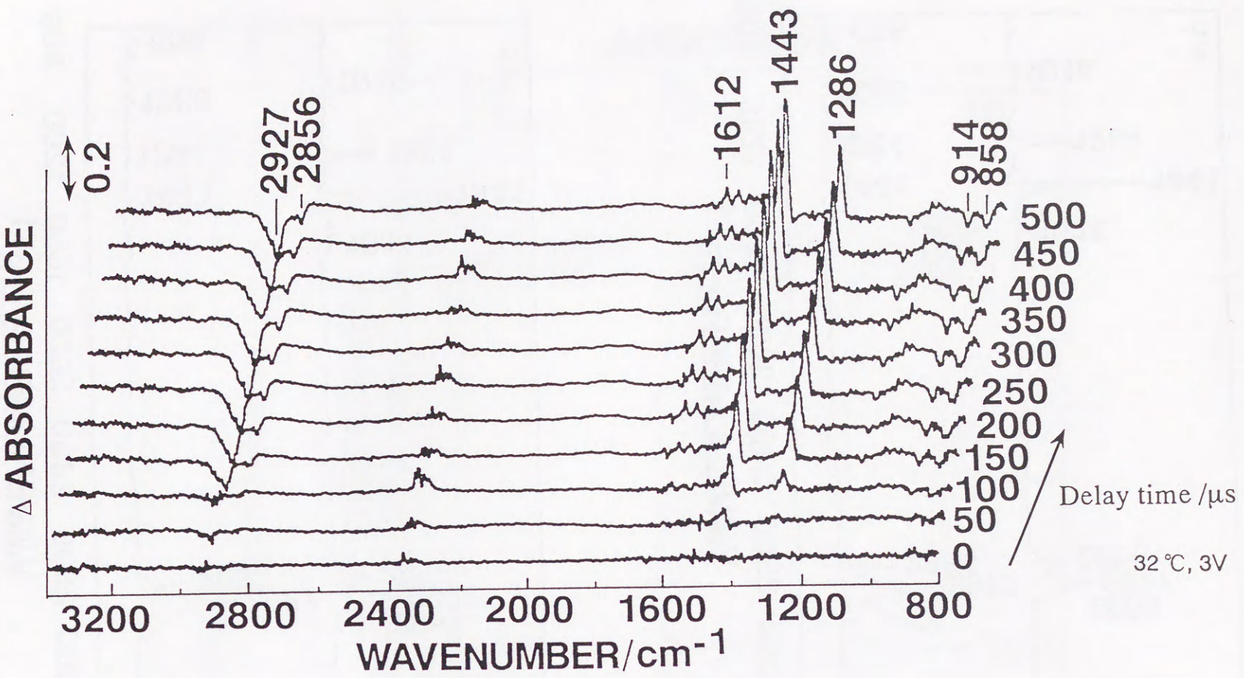


Figure 6. TRFTIR spectra of 8BPyO8(2F)* at 32 °C and ± 3 V.

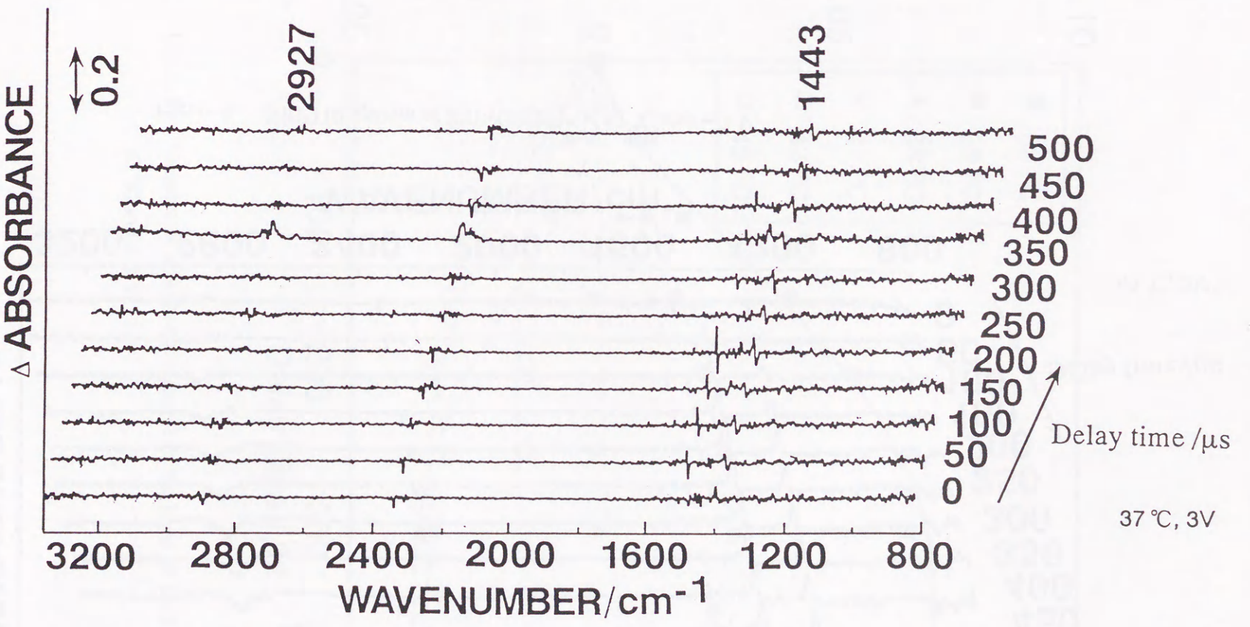


Figure 7. TRFTIR spectra of 8BPyO8(2F)* at 37 °C and ± 3 V.

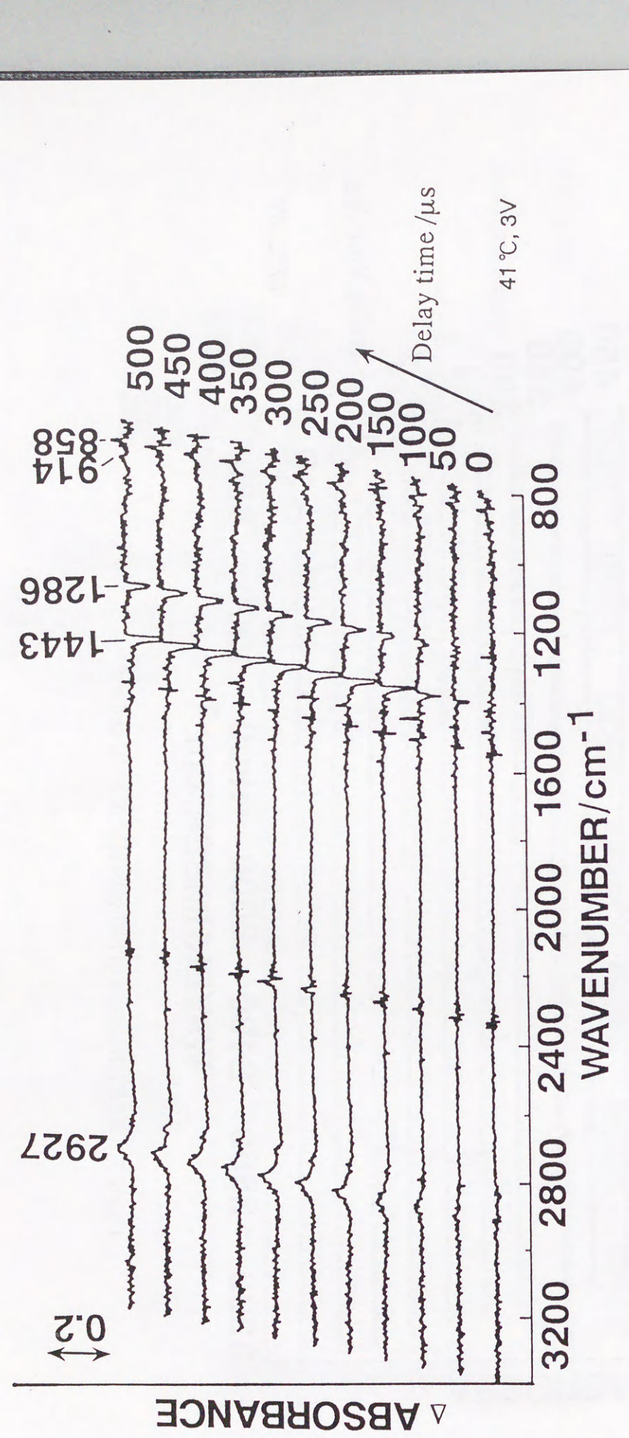


Figure 8. TRFTIR spectra of 8BPyO8(2F)* at 41 °C and ± 3 V.

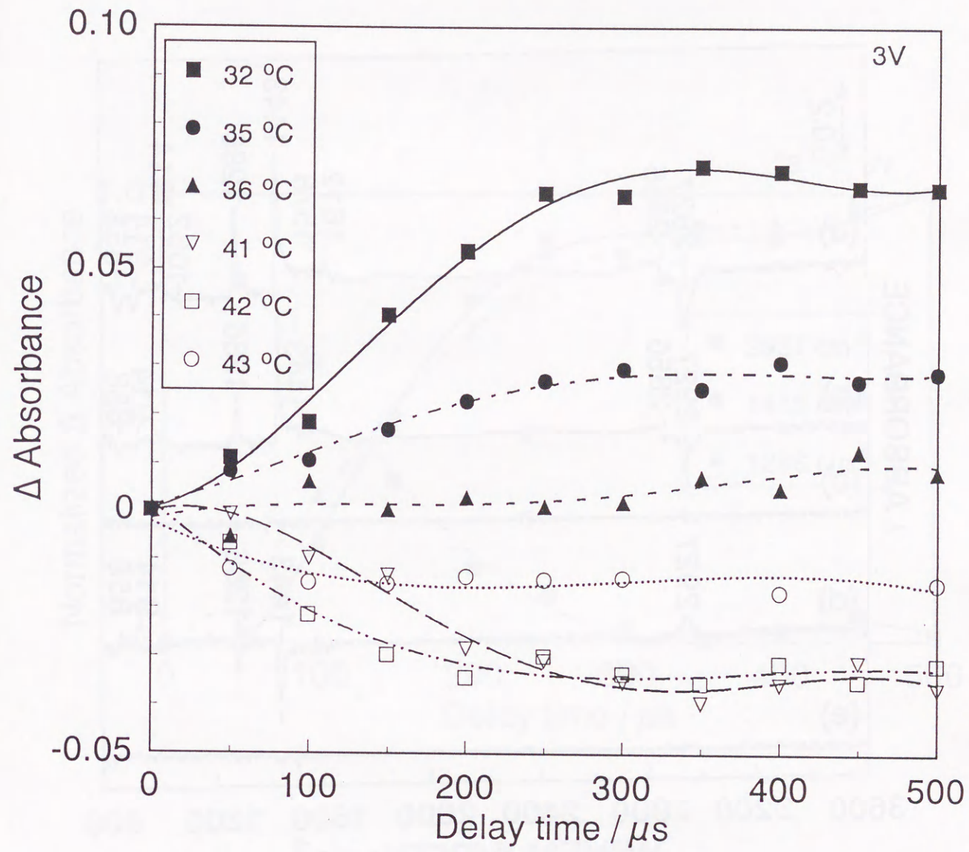


Figure 9. Variance of absorbance changes of the band at 1443 cm^{-1} measured at 32 - 43 °C and ± 3 V.

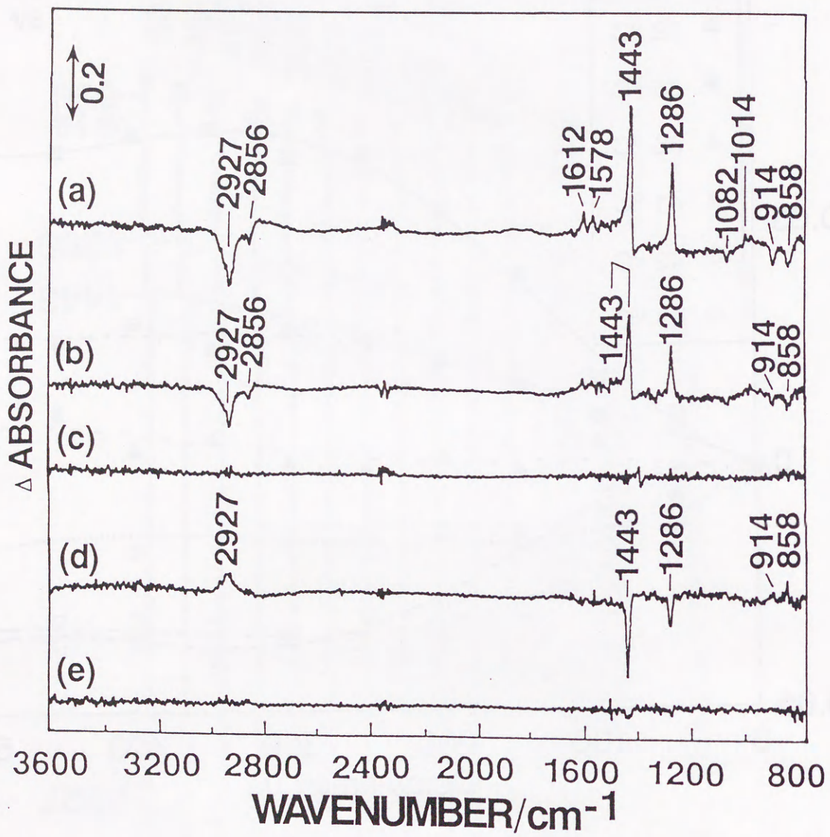


Figure 10. Comparison of the transient spectra of 500-μs delay measured at 32 - 44 °C and ± 3 V.

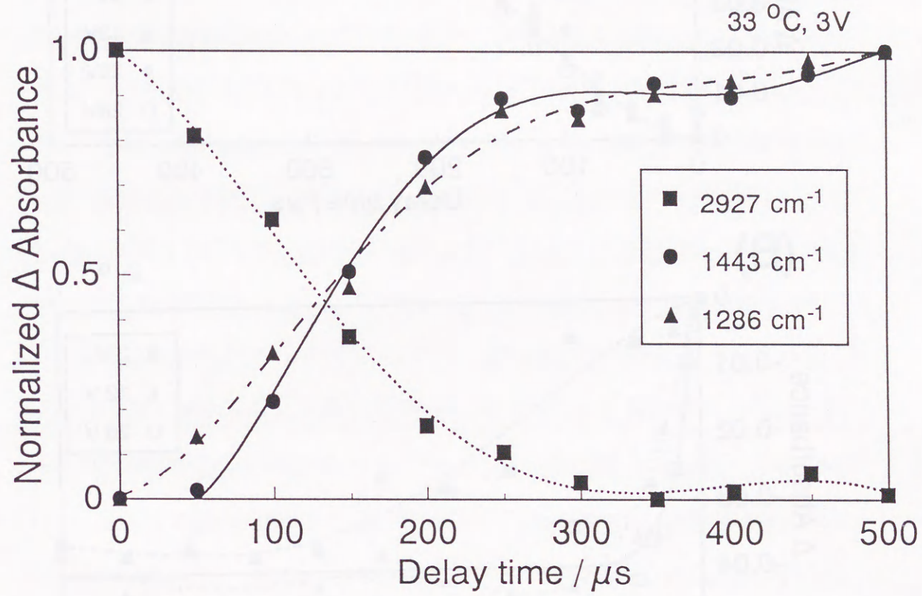


Figure 11. Variance of normalized absorbance changes measured at 33 °C and ± 3 V.

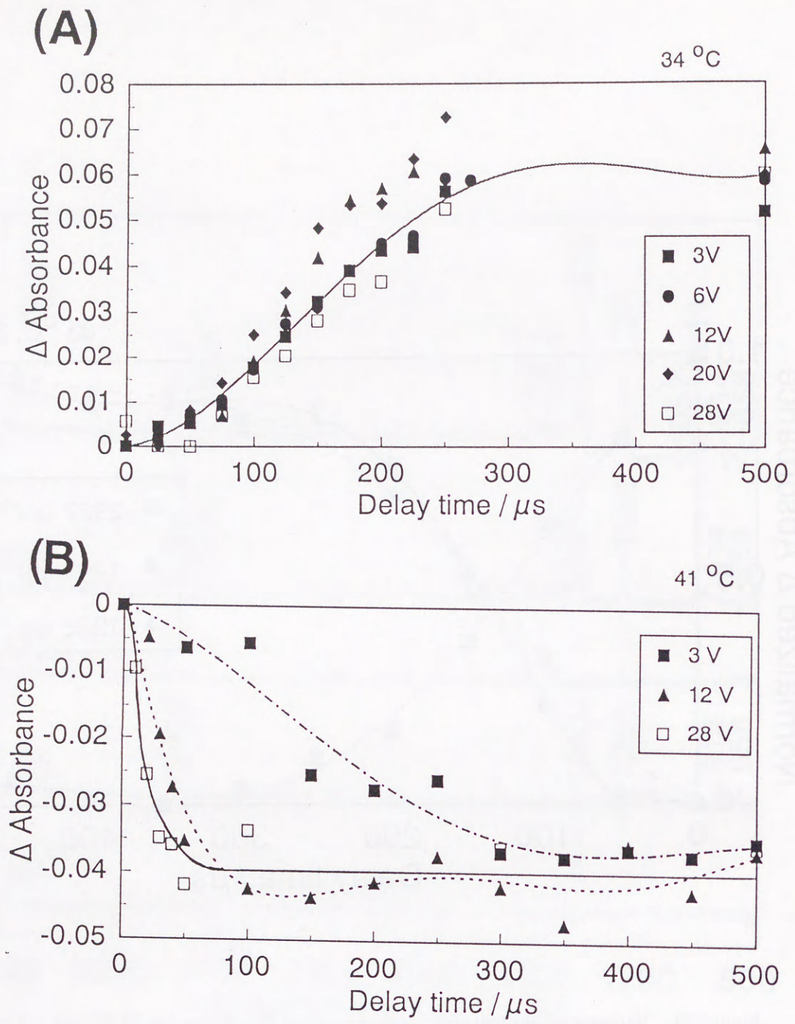


Figure 12. Variance of absorbance changes of the band at 1443 cm^{-1} measured at 34 °C (A) and 41 °C (B) and ± 3 - 28 V.

SECTION III-3: Sub-microsecond Preliminary Process of Electric-Field-Induced Reorientation of a Ferroelectric Liquid Crystal, 5-(2-Fluoroalkoxy)-2-(4-n-alkylphenyl)-pyrimidine, Studied by Time-Resolved Infrared Spectroscopy

ABSTRACT

Pulsed electric-field induced reorientation of a ferroelectric liquid crystal (FLC), 5-(2-fluorooctyloxy)-2-(4-hexylphenyl)-pyrimidine, has been investigated by using a dispersive sub-microsecond time-resolved infrared spectroscopic technique. The observed absorbance decay for a band at 1440 cm^{-1} due to a ring stretching mode of the phenylpyrimidine group indicates that the FLC molecule reorients from a stationary state with a slight delay (less than 1 μs) just after the upswing of the electric field, while counter-reorientation occurs with a delay time of a microsecond after the reverse of the electric field. The delay time for the counter-reorientation changes with temperature, indicating that the viscosity has a strong influence on the delay time. It is also indicated in the present study that the whole FLC molecule reorients simultaneously as a rigid rod in both preliminary and counter-reorientation process.

INTRODUCTION

In recent years, time-resolved infrared studies on liquid crystals (LCs) have aroused keen interest because the temporal responses of individual infrared bands provide solid information about the detailed reorientation dynamics of LCs [1-10]. An asynchronous time-resolved FT-IR technique has used to investigate the electric-field-induced reorientation of ferroelectric LCs (FLCs) in previous sections [7,9]. This technique is useful for infrared studies of time-dependent phenomena in the microsecond range. In the previous study on the chiral smectic C (C*) phase of 5-(2-fluorooctyloxy)-2-(4-octylphenyl)-pyrimidine (8BPyO8(2F)*), in which was found an inversion of the spontaneous polarization (Ps) with temperature change [11], we obtained the following conclusions [9]: (1) The LC molecule reorients from the perpendicular (zero time of delay) to parallel (500 μs delay) direction with respect to that of the polarized infrared light at 32 °C while it does reversely at 41 °C. (2) The change in the magnitude the voltage applied has little influence on the rate of reorientation in the region of the positive Ps while the rate in the region of the negative Ps strongly depends upon the voltage.

On the other hands, an ac-coupled dispersive time-resolved infrared technique has developed by Hamaguchi *et al*. [12-14]. Time resolution as high as 50 ns has been achieved with the minimum detectable change $\Delta A/A \sim 10^{-6}$ in the region 4000-700 cm^{-1} [14]. This technique has been

applied to the studies of the electric-field-induced reorientation of nematic LCs [4,6]. The multiplexing ability of the dispersive system in the time domain was demonstrated very clearly in these studies in which many temporal response curves of individual absorption bands were measured under a variety of conditions for the applied electric field [4,6].

In this section, the dispersive time-resolved infrared spectroscopy to a FLC, 5-(2-fluorooctyloxy)-2-(4-hexylphenyl)-pyrimidine (6BPyO8(2F)*; Figure 1) which also shows an inversion of the Ps with temperature change (Figure 1), was applied. The purpose of the present study is to explore further the mechanism of the electric-field-induced reorientation of the FLC in the sub-microsecond time scale.

EXPERIMENTAL

The sample of 6BPyO8(2F)* was synthesized by the procedure reported elsewhere [11]. A sample cell was assembled by the same method as that previously described [7]. The cell thickness was controlled to be 3.2 μm. The cell was put into a temperature control unit consisting of an OMRON E5T thermocontroller and a Peltier element described in previous section. This system guaranteed us a temperature control and stability of ± 0.1 °C at 50 °C. To obtain a good domain the cell was gradually cooled down (1 $Kmin^{-1}$) from the isotropic phase. The alignment of the FLC molecules was checked by microscopic polarized infrared measurement with a JIR-6500 (JEOL) FT-IR spectrometer. The microscopic instrument was used to confirm that the domain investigated was uniform. A wire grid polarizer was placed in front of the LC cell to obtain polarized infrared light; the axis of the polarizer was set parallel to the rubbing direction. The dichroic ratios for bands at 1440 and 2924 cm^{-1} at 44 °C were 6.53 and 1.47, respectively.

The rectangular pulse wave with voltage ± 5.0 V from a function generator (KENWOOD FG-273) was applied to the cell. The pulse widths of 5.0, 10.0, 20.0, and 300 μs with repetitions of every 230, 470, 920, and 3000 μs, respectively, were employed for the measurements.

Time-resolved infrared spectra (difference spectra) were recorded on an ac-coupled dispersive time-resolved infrared spectrometer previously reported [12-14]. The time resolution in both rise and decay

signals of an absorbance change is sub-microsecond. A digital sampling oscilloscope (Tektronix, 2430A) was employed for the measurement of the time response of a certain infrared band at a fixed wavenumber.

RESULTS AND DISCUSSION

Figure 2 shows temperature dependence of the absorbance change for a band at 1440 cm^{-1} assignable to a ring stretching mode of the phenylpyrimidine group [9]. This band, the strongest one in the difference spectra of the FLC molecule [9], is very suitable to probe dynamics of its core part. The pulse width and repetition of the electric field were 300 μs and 3 ms, respectively, and the temperature was changed in the range of 40-60 °C. To our best knowledge, the decay curves shown in Figure 2 are the best in terms of a signal-to-noise ratio among all the time-resolved infrared studies of FLCs reported previously [7-9,15]. This is by virtue of using the ac-coupled dispersive technique.

With the temperature change the absorbance change inverts its polarity; in the lower temperature range the delta absorbance is positive, *i.e.* the reorientation is from the perpendicular to parallel direction with respect to that of the polarized infrared light, while in the higher temperature range it is negative, *i.e.*, from the parallel to perpendicular direction. This result corresponds to the Ps inversion of this FLC molecule with temperature [11]; in the temperature region of positive Ps the rate and extent of reorientation increase with the decrease in the temperature, while in the region of negative Ps the rate increases with the increase in the temperature. Above 56 °C the absorbance change decreases sharply because of the phase transition to S_A. These results well agree with the measurements of the Ps, response time, and tilted angle reported previously [11].

In Figure 3 are shown the absorbance changes for the same band for the preliminary process at 41, 46, and 50 °C. The pulse width and repetition rate of the electric field were 10.0 μs and 470 μs, respectively. The reorientation from the stationary state starts with a slight delay (less than 1 μs) after the leading edge of the positive electric field pulse (at 0 μs), while the counter-reorientation occurs with a delay of more than 1 μs after the reverse of electric field (at 10 μs). This result shows that the FLC molecule is very sensitive to the electric field in the stationary state while it needs a rather larger time scale for the counter-reorientation. Of note is that the delay time for the counter-reorientation is temperature dependent.

The results of higher time-resolution measurements of the decay at 46 °C and 55 °C are presented in Figure 4. The pulse width and repetition rate of the electric field were 5.0 μs and 230 μs, respectively. Figure 4 clearly demonstrates the temperature dependence of the counter-reorientation. The delay time for the counter-reorientation at 55 °C is shorter than 1.0 μs. At this temperature the delay time for the reorientation from the stationary state is about 0.3 μs and the reorientation velocity is much higher compared with that at 46 °C. According to theoretical calculation [16], the response time for the reorientation, τ, is proportional to the viscosity, η, and inversely proportional to spontaneous polarization, Ps, and electric field, E. The results obtained in this study indicate that this theoretical consideration can also be applied to dynamics in the preliminary process of the

reorientation. Suppose that there is a rotating rigid rod, the presence of a time delay in the counter reorientation could be interpreted in terms of a moment of inertia. The delay time would then be a function of the viscosity, the angular velocity of the reorientation, and the moment of inertia. The viscosity, the angular velocity, and the moment of inertia should be correlated with the temperature, electric field, and the chemical structure of the FLC molecule, respectively. Considering that the latter two factors are constant in the present experiment, the observed changes in the delay time for the counter-reorientation may be ascribed to the change in the viscosity.

Figure 5 illustrates the absorbance changes of the band at 1440 cm^{-1} between 5.0 and 10.0 μs of pulse width measured at 46 °C. The delay of the counter-reorientation is about 1.7 μs in both pulse width, indicating that the pulse width has little influence on the delay time of the counter-reorientation. The angular velocity (the velocity of rotation to a molecule) of the reorientation is almost constant during those time delays.

In Figure 6 are compared the absorbance changes for three major bands at 1440, 1284, and 1086 cm^{-1}. The bands at 1284 and 1086 cm^{-1} are assigned to an antisymmetric stretching mode of the ring-O-C group and the C-F stretching mode, respectively. The pulse width and repetition rate of the electric field were 5.0 and 230 μs, respectively, and the temperature was 45 °C. The delay time and shape of these three curves are very similar to one another, indicating that the core part of the FLC molecule reorients simultaneously even in the process of counter-

reorientation. Although the C-F group is considered to be the most essential part for the appearance of the polarization, the result obtained here suggests that the entire core is equally sensitive to the electric field. The results also suggest that the same mechanism is applicable to both the normal and counter-reorientation.

Figure 7 illustrates the absorbance changes for a band at 2928 cm^{-1} due to a CH_2 antisymmetric stretching mode. This band was so weak in the time-resolved difference spectra that an electric field with the pulse width of 20.0 μs and repetition of 920 μs was employed. The delay times for the counter-reorientation are 1.2-1.7 μs, very close to those of the bands arising from the core part (Figure 3). Contrary to the expectation that the hydrocarbon chains have some conformational flexibility and little sensitivity to the electric field, the present result indicates that the whole FLC molecule reorients simultaneously as a rigid rod even in the case of counter-reorientation process, at least within the time resolution of this study. The hydrocarbon chains must receive a force working against their own inertial force from the core part.

CONCLUSION

The present study has demonstrated that the ac-coupled dispersive time-resolved infrared technique is powerful in investigating the preliminary and counter reorientation process of the FLC molecule induced by a pulsed electric field. The same experiment, if undertaken with an asynchronous FT-IR apparatus, would have been prohibitively difficult. The following conclusions can be reached from the present study: (1) The reorientation of the FLC molecule from the stationary state takes place with a slight delay (less than 1 μs) after the leading edge of the positive electric field pulse, whereas the counter-reorientation occurs with a delay of more than 1 μs after the reverse of the electric field. (2) The delay time for the counter-reorientation is temperature-dependent, and it seems that the viscosity is an important factor determining the delay time. (3) The whole FLC molecule reorients simultaneously as a rigid rod even in the case of counter-reorientation process, and the same mechanism of the reorientation seems to be applicable to both the preliminary and counter-reorientation.

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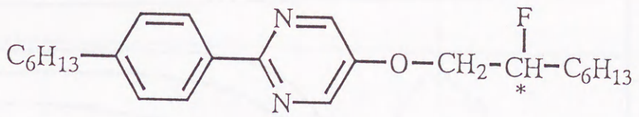
(A)



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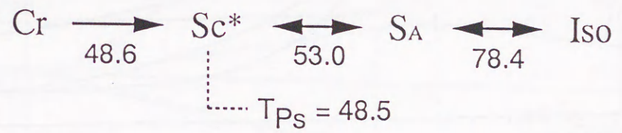

Figure 1. Chemical structure (a) and phase transitions (b) of 6BPyO8(2F)*. This compound shows a Ps inversion at 48.5 °C.

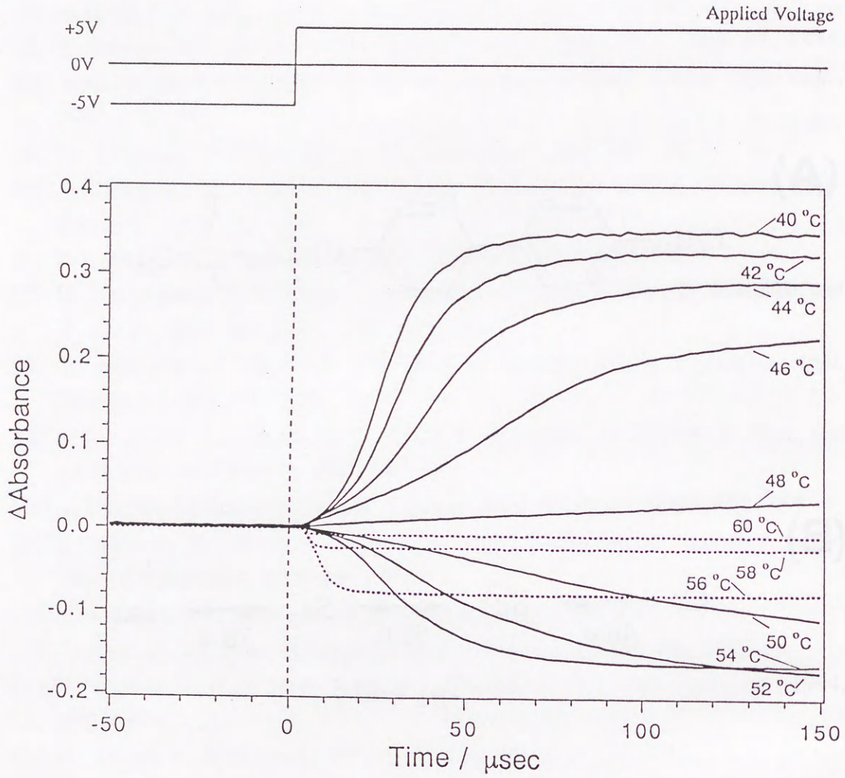

Figure 2. Temperature dependence of the absorbance change for the band at 1440 cm^{-1} in the long delay time scale. The pulse width and repetition rate of the electric field were 300 μs and 3 ms, respectively.

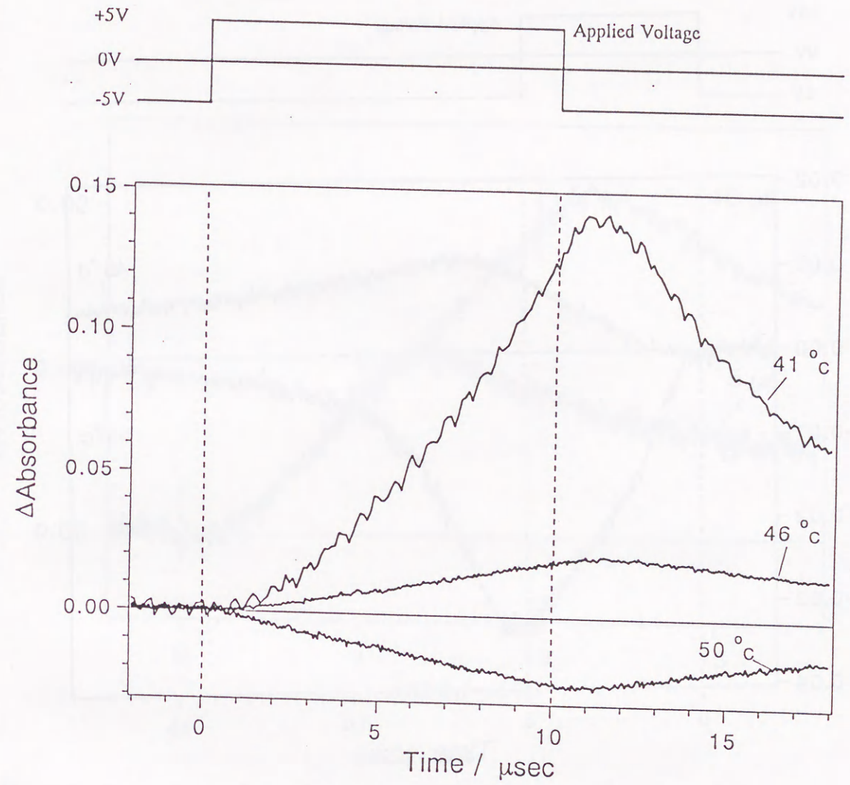

Figure 3. Absorbance change of the 1440 cm^{-1} band at 41, 46, and 50 °C. The pulse width and repetition rate of the electric field were 10.0 and 470 μs, respectively.

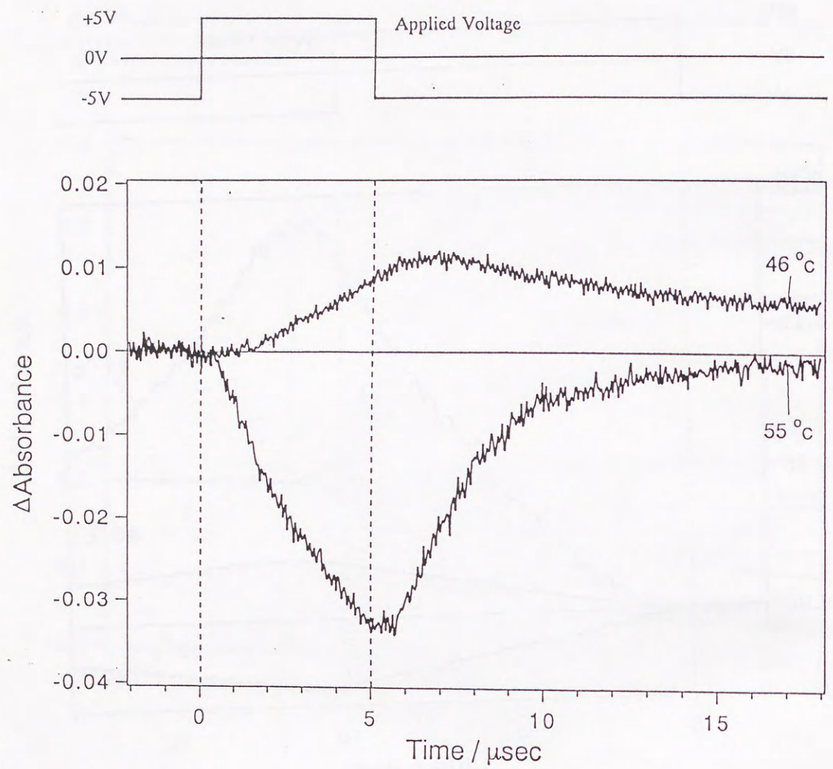

Figure 4. Absorbance change of the 1440 cm^{-1} band at 46 and 55 °C. The pulse width and repetition rate of the electric field were 5.0 and 230 μs, respectively.

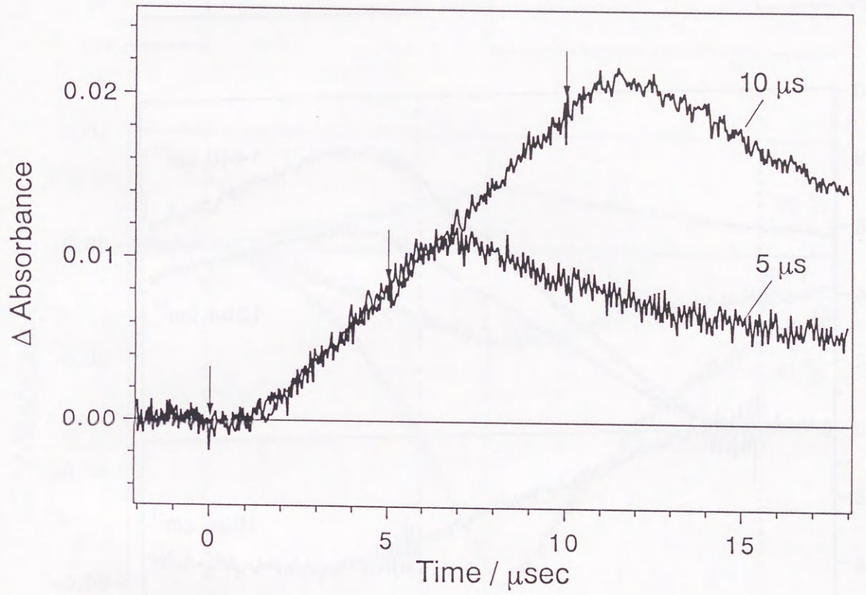

Figure 5. Comparison of absorbance change of the 1440 cm^{-1} band between 5.0 and 10.0 μs pulse width measured at 46 °C.

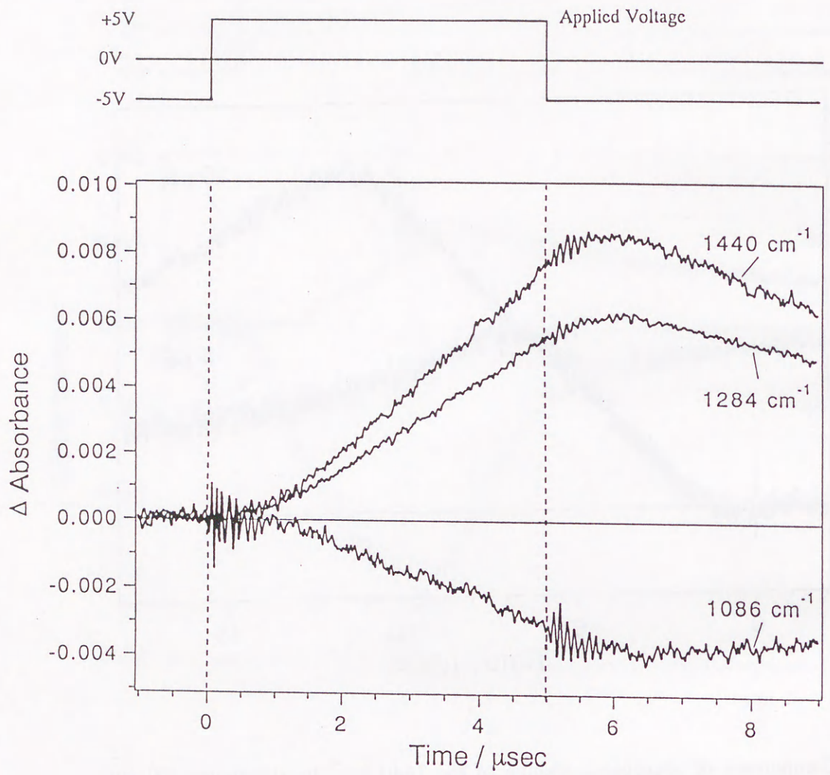

Figure 6. Absorbance changes for major bands at 1440, 1284, and 1086 cm^{-1} due to the core part. The pulse width and repetition rate of the electric field were 5.0 μs and 230 μs, respectively, and temperature was 45 °C.

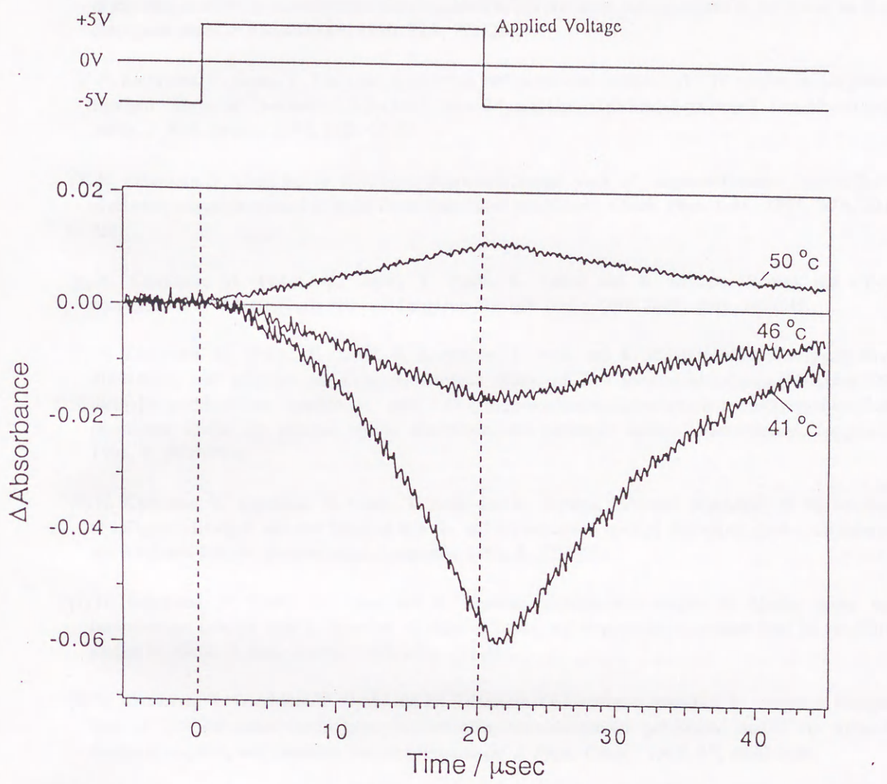

Figure 7. Absorbance change of the 2928 cm^{-1} band from the hydrocarbon chains. The pulse width of 20.0 μs and repetition rate of 230 μs were employed.

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